Biogeosciences
Discussions

Magnetic quantification of Fe and S bound as magnetosomal greigite in laminated sapropels in deeper basins of the Baltic Sea

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Abstract

Magnetotactic bacteria (MTB) biomineralize magnetite and/or greigite for navigation purposes and it have been suggested that their magnetosomes make a significant contribution to the burial of Fe (and S and O) in sedimentary environments. To test this hypothesis and improve our understanding of MTBs impact on the rate of burial of these two elements we have quantified the abundance of Fe and S bound as greigite magnetofossils in laminated Baltic Sea sapropels, which were formed during periods of hypoxia and anoxia, using mineral magnetic measurements. Fluxes of Fe and S in the form of preserved greigite magnetofossils were calculated for three sedimentary sequences. The magnetosomal Fe (and S) fluxes range between 0.19 and $1.46 \times 10^{-6}\,\mathrm{g\,cm^{-2}\,yr^{-1}}$ (0.15 and $1.12 \times 10^{-6}\,\mathrm{g\,cm^{-2}\,yr^{-1}}$), and varied in time and space. The contribution of magnetosomal Fe to total Fe fluxes is relatively low, $< 0.2\,\%$, although its contribution can be important in other stratified waters that suffer from hypoxia/anoxia. We show that the magnetosomal fluxes of Fe in the Baltic Sea are, however, similar to fluxes of Fe derived from mineral magnetic studies of magnetite magnetosomes in organic rich, varved freshwater lake sediments in Sweden.

1 Introduction

Microbial metabolic processes are known to drive a variety of biogeochemical elemental cycles (Falkowski et al., 2008). Knowledge of the rates of mineral production and preservation caused by biologically controlled mineralization (BCM) and biologically mediated mineralization (BMM) contributes to our understanding of the impact of microbes on these cycles and, from a geological perspective, the storage of elements caused by sedimentation and long-term burial. The presence of minerals in forms that are diagnostic of past microbial activity in geologic media provides the opportunity to assess their role in specific element cycles if fluxes can be quantified with suitable precision.

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Magnetotactic bacteria (MTB) are a diverse group of prokaryotes that produce intracellular ferrimagnetic minerals (magnetite and/or greigite), primarily for geomagnetic orientation as they search for optimal growth conditions within the oxic-anoxic transition zone (OATZ) in chemically stratified water columns or the uppermost sediments (Lefèvre and Bazylinski, 2013). Most cultured species grow chemolithoautotrophically by using reduced sulphur compounds or chemoorganoheterotrophically by consuming organic acids (Lefèvre and Bazylinski, 2013). MTB can, therefore, use several sources for food and energy depending on the prevalent environmental conditions and they have been found in many different environments such as lakes, seas, salt ponds and marshlands. A general consensus is that the magnetite producing MTB live at the OATZ while the greigite producing MTB live in reducing environments, such as the sulphidic anoxic zone below the OATZ.

While knowledge of the genetic diversity of MTB is increasing significantly (Lefèvre and Bazylinski, 2013) very few quantitative studies of the influence of MTB on biomineralization rates and burial of the distinct ferrimagnetic minerals they produce are available. Simmons and Edwards (2007) reported that magnetosomal Fe represented 0.5–5 % of the iron sulphide flux in the deep basin of the Black Sea and between 1.3–13 % in the Pettaquamscutt estuary. They hypothesise a potential role for MTB in Fe fluxes in other similarly chemically stratified basins and that MTB should be considered as important contributors to the Fe flux in these environments.

Under suitable circumstances the ferrimagnetic properties of the diagnostic single-domain grains produced by MTB allow the mineral concentrations to be quantified using magnetic methods (Lascu et al., 2010). Reinholdsson et al. (2013) demonstrated that enhanced mineral magnetic concentrations in laminated Baltic Sea sapropels is due to the presence of magnetosomal greigite (Fe_3S_4), which causes the ferrimagnetic mineral concentration to be approximately one order of magnitude higher in the laminated sapropels compared to the non-laminated sediments. This relatively high degree of magnetic enhancement in the Baltic Sea is due to the generally low magnetic susceptibility of surrounding sources of clastic minerals and this case provides an excellent

opportunity to use magnetic methods to quantify the impact of greigite synthesising MTB on the flux of Fe and S to sediments and the burial of Fe and S in the form of magnetosomes. Another advantage of a geophysical approach to quantify MTB influence on BCM is that greigite oxidizes rapidly on exposure to the atmosphere (Snowball and Thompson, 1988), with the result that valuable information about greigite magnetosome mineralization can be lost during core storage, sampling and analytical preparation (Reinholdsson et al., 2013). Magnetic measurements are rapid, non-destructive and require minimal sample preparation.

In this paper, we test the Simmons and Edward's (2007) hypothesis by calculating magnetosomal Fe (and S) fluxes in laminated Baltic Sea sapropels, using mineral magnetic measurements as a basis for their quantification.

2 Study area: the Baltic Sea

The Baltic Sea is a semi-enclosed basin with its only connection to the North Sea via the shallow Belt Seas and the narrow Öresund Strait in the south-west. Due to isostatic uplift of the crust and eustatic global sea level changes the Baltic Sea has undergone major environmental changes since the last deglaciation. The history of the Baltic Sea has been divided into four major phases: the Baltic Ice Lake, the Yoldia Sea, the Ancylus Lake and the Littorina Sea. The transition into the latest phase, the Littorina Sea, was gradual and started ca. 8500–8000 yr ago (Björck, 2008) when saline water from the North Sea entered the basin via the Kattegat and Skagerrak and ended the freshwater Ancylus Lake stage.

Modern hydrographical settings include two salinity gradients, one horizontal and one vertical. Saline water inflows from the south-west create a north-south gradient with less saline water in the north, where there is also significant freshwater input from river systems. The saline inflows also create a depth gradient (a halocline) with denser more saline water close to the bottom. This halocline prevents vertical mixing between oxic surface waters and bottom waters, which can result in benthic hypoxia or anoxia. In

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this situation no bioturbation occurs and laminated sediments, which are magnetically enhanced, are preserved.

Sediments deposited during the Littorina Sea stage in the deeper basins ($> 80\,\mathrm{m}$ water depth) are characterized by alternating non-laminated and laminated sediments, representing oxic and hypoxic/anoxic bottom water conditions, respectively. The laminated sediments are organic rich (sapropels) and are deposited during warmer periods represented by the Holocene Thermal Maximum (HTM), the Medieval Warm Period (MWP), and the last $\sim 200\,\mathrm{yr}$ (Zillen et al., 2008). The cause of the more recent occurrence of sapropels may be a combination of human induced eutrophication and climate change since the European Little Ice Age (Conley et al., 2009; Zillen et al., 2008).

3 Material and methods

3.1 Core collection and sample preparation

During three research cruises in 2009 and 2010 sediments were recovered at three stations in the Baltic Sea (Fig. 1). Site LL19 ($20°18'39.00''$ E $58°52'50.40''$ N at $169\,\mathrm{m}$ water depth) is situated in the north central Baltic Proper. Site F80 ($19°53'48.60''$ E $58°0'0.00''$ N at $181\,\mathrm{m}$ water depth) is situated in the Fårö Deep and LZGB2 ($17°49'51.72''$ E $58°21'31.62''$ N at $110.5\,\mathrm{m}$ water depth) is located in the western Gotland Basin. The cores, which are named after the localities, were retrieved with a $6\,\mathrm{m}$ long gravity corer with an internal plastic liner of $10\,\mathrm{cm}$ diameter (LL19, F80) or $12\,\mathrm{cm}$ (LZGB2). After retrieval they were divided into $1\,\mathrm{m}$ sections, which were sealed with end-caps and stored at $4\,°\mathrm{C}$ before transportation. At Lund University they were split longitudinally into two halves and a visual description was made. To obtain samples for mineral magnetic measurements the sediment cores were sampled at contiguous $1\,\mathrm{cm}$ intervals into discrete cubic plastic boxes (internal volume $\sim 7\,\mathrm{cm}^3$). The residual at each level was sampled into a larger plastic box and freeze-dried for loss on igni-

tion (LOI) measurements. Subsequent analyses were performed at the Department of Geology, Lund University, if not stated otherwise.

3.2 Mineral magnetic measurements

The mineral magnetic properties of LL19 and F80 were published by Reinholdsson et al. (2013), which indicate that the concentration of ferrimagnetic minerals can be adequately quantified by measuring the saturation isothermal remanent magnetization (SIRM) at room temperature. The discrete samples taken from LZGB2 were subjected to a magnetic field of 1 Tesla (T) in a Redcliffe 700 BSM pulse magnetiser. The induced SIRM was subsequently measured with a Molspin Minispin magnetometer.

3.3 Loss-on-ignition (LOI) measurements

LOI values for LL19 and F80 were published by Reinholdsson et al. (2013). To estimate the organic matter content for LZGB2 the LOI was measured according to the methods described by Heiri et al. (2001). Approximately 0.5 g of each sample was placed in small crucibles and air-dried at 105 °C overnight. After weighing, the samples were heated for 4 h at 550 °C and the LOI calculated as the % weight loss caused by ignition.

3.4 Magnetosomal iron and sulphur calculations

Theoretically, the amount of Fe and S in the sediments bound as magnetosomal greigite can be calculated based on the SIRM data after a correction is made for the contribution of non-magnetosomal components of the magnetic mineral assemblage (input data in Table A2 in the Supplement). The calculations are based on SIRM data from laminated Littorina Sea sapropels. We applied Eqs. (3) and (6) from Lascu et al. (2010) to calculate the amount of Fe and S on a sediment dry weight basis. Our calculations are based on single-domain theory (Stoner and Wohlfarth, 1948), which states that $M_{RS}/M_S = 0.5$ for an assemblage of non-interacting grains, and the room temperature ferrimagnetic saturation magnetization (M_S) (μ_{ferri}), which has been measured as

$59\,A\,m^2\,kg^{-1}$ for greigite (Chang et al., 2008). The calculations allow us to derive the amount of magnetosomal greigite per unit mass. The amount of Fe and S can be determined from the relative abundance of Fe and S in greigite (Fe_3S_4) and their atomic weights. The calculated concentrations of greigite, Fe and S in each sample were converted to units of flux using the time–depth relationships established by Lougheed et al. (2012) and the sediment volumes and weights (Appendix B).

3.5 Core chronology

Lougheed et al. (2012) published an age model for sediment sequences from the Gotland Deep that is based on palaeomagnetic secular variation (PSV) and lead (Pb) isochrones, which they transferred to the nearby site of 372740-3 ($20°15'18.00''$ E, $57°23'6.00''$ N) under the assumption of common temporal development in LOI. The same geochronology and LOI correlation method were applied by Jilbert and Slomp (2013) to cores recovered from sites F80 and LL19. Likewise, we used common tie-points (7–11) in LOI trends in 372740-3 to transfer the geochronology of Lougheed et al. (2012) to our cores that were recovered from sites LL19, F80 and LZGB2 and applied linear interpolation between these to obtain ages for the sampled levels.

The presented annual flux rates should be considered as a mean over centuries or millennia since the precision of the chronology does not allow us to state the variability of sediment accumulation within periods less then ca. 100 yr.

4 Results

4.1 Sediment stratigraphy

The stratigraphic units in sediment cores LL19 (538 cm long), F80 (403 cm long) (Reinholdsson et al., 2013) and LZGB2 (480.5 cm long) (Table A3) were classified according to their visual and mineral magnetic properties by Reinholdsson et al. (2013). In sum-

mary, sediment cores LL19 and LZGB have grey clay (Ancylus Lake clay) interbedded with black bands (1–2 cm thick) and large (∼ 1 cm) black nodules in the lower sediments (373–538 cm in LL19 and 315–480.5 cm in LZGB2). They both have a gradual transition into sediments that characterise the onset of the Littorina Sea phase. All three sedi-
5 ment cores cover the Littorina Sea phase with the characteristic intervals of laminated sapropels (units C and E) and non-laminated sediments (unit D). Zillén et al. (2008) established that the laminated units formed during periods of relatively warm climate, notably the Holocene Thermal Maximum (HTM) ca. 9000–5000 cal yr BP and the Medieval Warm Period (MWP) ca. 1200–750 cal yr BP.

4.2 Fe and S bound as magnetosomal greigite in Baltic Sea sapropels

The concentrations of Fe and S have been calculated for the three Baltic Sea sediment cores (Table A1). The SIRM (corrected for background level) (Table A2) values vary within sediment cores but also between cores, resulting in variations in the concentration of magnetosomal bound Fe and S. For the MWP the Fe (S) concentrations range
15 between 28 and 90×10^{-3} (22 and 69×10^{-3}) $g\,kg^{-1}$ sediments, while the values for the HTM range between 37 and 108×10^{-3} (28 and 82×10^{-3}) $g\,kg^{-1}$ sediments.

The fluxes of magnetosomal Fe and S for the three sediment cores are limited by the range of the age model, which is restricted to the period ca. 640–6400 cal yr BP (we do not extrapolate accumulation rates below the lowest dated level). Therefore some
20 laminated parts are excluded from the flux calculations. Magnetic grain size parameters based on magnetic remanence, such as χ_{ARM}/SIRM, in sediment cores F80 and LL19 do not detect the presence of magnetosomes in the non-laminated parts (Reinholdsson et al., 2013), and therefore magnetosomal Fe flux calculations are restricted to the laminated sections (i.e. HTM and MWP). The mean values of the Fe and S fluxes to
25 the laminated sapropels, which are illustrated in Fig. 2, are similar in the F80 (Fe = 0.91, S = 0.70×10^{-6} $g\,cm^{-2}\,yr^{-1}$) and LZGB2 (Fe = 0.89*, S = 0.68×10^{-6} $g\,cm^{-2}\,yr^{-1}$) sediment cores and relatively lower in LL19 (Fe = 0.50*, S = 0.40×10^{-6} $g\,cm^{-2}\,yr^{-1}$).

The magnetosomal Fe flux (Table 1, Fig. 2) ranges between 0.19–$1.46 \times 10^{-6}\,\mathrm{g\,cm^{-2}\,yr^{-1}}$ for the MWP and between 0.45–$1.11 \times 10^{-6}\,\mathrm{g\,cm^{-2}\,yr^{-1}}$ for the HTM time period. The magnetosomal S fluxes ranges between 0.15–$1.12 \times 10^{-6}\,\mathrm{g\,cm^{-2}\,yr^{-1}}$ for the MWP and between 0.35–$0.85 \times 10^{-6}\,\mathrm{g\,cm^{-2}\,yr^{-1}}$ for the HTM time period. In the MWP the only major difference is that F80 (Fe = 1.46, S = $1.12 \times 10^{-6}\,\mathrm{g\,cm^{-2}\,yr^{-1}}$) is higher than LZGB2 (Fe = 0.19, S = $0.15 \times 10^{-6}\,\mathrm{g\,cm^{-2}\,yr^{-1}}$). LL19 have intermediate fluxes for Fe $0.64 \times 10^{-6}\,\mathrm{g\,cm^{-2}\,yr^{-1}}$ and S $0.49 \times 10^{-6}\,\mathrm{g\,cm^{-2}\,yr^{-1}}$. LZGB2 (Fe = 1.11, S = $0.85 \times 10^{-6}\,\mathrm{g\,cm^{-2}\,yr^{-1}}$) have higher fluxes in the HTM than both LL19 (Fe = 0.45, S = $0.35 \times 10^{-6}\,\mathrm{g\,cm^{-2}\,yr^{-1}}$) and F80 (Fe = 0.70, S = $0.54 \times 10^{-6}\,\mathrm{g\,cm^{-2}\,yr^{-1}}$) which are similar.

The LZGB2 core has significantly higher magnetosomal S and Fe fluxes in the HTM time period ($1.11 \times 10^{-6}\,\mathrm{g\,Fe\,cm^{-2}\,yr^{-1}}$) than in the MWP ($0.19 \times 10^{-6}\,\mathrm{g\,Fe\,cm^{-2}\,yr^{-1}}$). The opposite trend is found in the F80 sediment core, which has higher fluxes in the MWP ($1.46 \times 10^{-6}\,\mathrm{g\,Fe\,cm^{-2}\,yr^{-1}}$) compared to the HTM ($0.70 \times 10^{-6}\,\mathrm{g\,Fe\,cm^{-2}\,yr^{-1}}$). The sediment core LL19 shows only a small difference in fluxes from the MWP compared to the HTM (0.64 and $0.45 \times 10^{-6}\,\mathrm{g\,Fe\,cm^{-2}\,yr^{-1}}$, respectively).

5 Discussion

The fluxes of Fe and S bound as magnetosomal greigite have been calculated based on mineral magnetic parameters and knowledge of the sediment accumulation rate. Although the magnetosomes were most likely produced in the water column, the calculated fluxes should perhaps be interpreted as reflecting the amount of magnetosomal greigite that has survived deposition and burial. The initial production might have been more since magnetosomes can be degraded during transport through the water column, for example in the acid vacuoles of grazing protozoa (Martins et al., 2007).

Our calculated magnetosomal fluxes of Fe and S may also be affected by the presence of the sodium (Na) that was evident in the TEM-EDX spectra of the magnetosomal greigite found in Baltic Sea sediments (Reinholdsson et al., 2013). The origin of the Na

(up to 10 %) is unknown. If the Na is a crystal component of the greigite magnetosomes there will be an error to the flux calculations since these are based on the relative abundances of Fe and S (3 : 4) and the addition of elements to the lattices of ferrimagnetic minerals tends to alter the value of saturation magnetisation that underpins the mag-
5 netic method, but the effects of impurities in greigite remain to be understood.

5.1 What is the contribution of magnetosomal greigite to the total and reactive Fe flux in the Baltic Sea sapropels?

Total Fe (Fe_T) data from sediment core F80 (Tom Jilbert and Caroline Slomp, unpublished) were transferred into Fe_T fluxes using the same methods as for calculating
10 the magnetosomal Fe fluxes. The Fe_T flux is $\sim 11 \times 10^{-4}\,g\,cm^{-2}\,yr^{-1}$ in the MWP and $\sim 9 \times 10^{-4}\,g\,cm^{-2}\,yr^{-1}$ in the HTM. A comparison between the Fe_T and the amount of Fe bound as magnetosomal greigite suggests that 0.19 % of the Fe_T originates from magnetosomal Fe in the MWP and 0.09 % in the HTM period. These values imply that the contribution of magnetosomal Fe is low compared to the total amount of iron
15 (~ 6.8 % for laminated sapropels), which is almost equivalent to the average amount of Fe (5 %) in Earth's crust (Lutgens and Tarbuck, 2000). It might be a better measure to compare the magnetosomal Fe to the reactive part of the iron pool (Fe_R), since this part is available to the biological system.

In laminated sediments from the Archipelago Sea Virtasalo and Kotilainen (2008)
20 calculated the component accumulation rate (CAR) of Fe that was extracted by a citrate-dithionite-bicarbonate solution, Fe_{CDB} (Slomp et al., 1996) which is assumed to be a measure of the Fe_R. For core AS5-PC2 the CARs of Fe_{CDB} range between 4 and $12 \times 10^{-6}\,mol\,cm^{-2}\,yr^{-1}$ which is equivalent to 2.2–$6.7 \times 10^{-4}\,g\,cm^{-2}\,yr^{-1}$ (Table 2). The magnetosomal Fe from the Baltic Sea laminated sapropels range from 0.19–
25 $1.46 \times 10^{-6}\,g\,cm^{-2}\,yr^{-1}$ and corresponds to 0.03–0.7 % of the Fe_R in the Archipelago Sea. These numbers also suggests that the contribution of magnetosomal Fe to the accumulation of Fe_R in Baltic Sea sediments is relatively low. There is, however a differ-

ence in location environment for the two compared datasets. The AS5-PC2 sediment core is retrieved from a shallower depth (33 m) compared to LL19, F80 and LZGB2, which are recovered from deeper basins, 110.5–181 m water depth. A shallower location, situated closer to land, which is the case for AS5-PC2, should receive relatively more clastic matter than locations further away from land, such as the deeper basins. Thus, compared to AS5-PC2, the Fe_R would be lower in the deeper sites of LL19, F80 and LZGB2 and the relative contribution of magnetosomal Fe to the Fe_R accumulation rate would increase in the latter sites.

5.2 Possible explanations to changes in magnetosomal Fe fluxes in Baltic Sea sapropels

Roberts et al. (1999) found that the degree of magnetic enhancement in eastern Mediterranean sapropels of Pliocene to Holocene age, which Reinholdsson et al. (2013) argue was probably caused by magnetosomal greigite, was positively correlated to the organic carbon content ($R^2 > 0.75$). Similarly, the magnetic enhancement of the Baltic Sea sapropels are, in general, positively correlated to higher LOI (Reinholdsson et al., 2013). However, on closer inspection, the ferrimagnetic concentration does not have a perfect positive linkage to the LOI data since the R^2 values are only 0.01 and 0.54 (SIRM vs. LOI% from laminated sapropels in Ll19 and F80, respectively). The flux of Fe bound in greigite magnetofossils, which have been identified in the laminated sapropels, does not have a good link to the LOI%, the LOI-flux or the sediment accumulation rate ($R^2 = 0.02$–0.32) for the sediment cores LL19 and F80. The LOI flux and the sediment accumulation rate are positively correlated to each other, with R^2 values that range between 0.38 and 0.73 (Fig. 3). This relationship suggests that the production and deposition of organic matter exerts a strong positive influence on the rate of sediment accumulation. This result contrasts with that of Jilbert and Slomp (2013) who based their conclusions on a regression between sedimentation rate and % LOI, rather than the flux. The concentration of magnetosomes, as inferred from the mineral magnetic data, does not co-vary with accumu-

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lation rate, which implies that magnetosomal Fe flux is not an artefact of dilution by a non-magnetic constituent. The accumulation rate and the LOI flux do not co-vary with the magnetosomal Fe flux, but there might be a connection between the parameters. As noted, the accumulation rate increases when the LOI flux increases, as for example at ∼ 4500 cal yr BP in core LL19 (Fig. 4). At the same time the magnetosomal Fe flux also increases. This pattern is also valid for sediment core F80. However, the subsequent decrease in these parameters does not co-vary, since LOI flux starts to decrease earlier then the Fe flux. This lag cannot be explained with the available data, but it is known that MTB are able to adapt their metabolism to environmental change: if necessary chemoorganoheterotrophic bacteria, which grow using organic acids, become chemolithoautotrophic and survive on reduced sulphur compounds (Lefèvre and Bazylinski, 2013). There is also the possibility that the MTB population is composed of different species, and that the relative amounts of these species change over time. One can hypothesise that chemoorganoheterotrophs dominate the MTB population during periods of high primary production and that the chemolithoautotrophs survive better when the primary production decreases and organic matter decomposition produces relatively more reduced sulphur compounds.

The pattern of an initial increase in organic matter production (as indicated by increased LOI flux) with the following increase in magnetosomal Fe flux does not fit the LZGB2 sediment core. This core has a positive correlation between the magnetosomal Fe flux and LOI% and LOI fluxes (R^2 = 0.55–0.63). One difference between the LZGB2 core and the F80 and LL19 core is their location within the Baltic Sea. Sites F80 and LL19 are situated in deeper basins in the eastern and northern Gotland Basin respectively while LZGB2 is located at shallower water depth in the western Gotland Basin (Fig. 1). Our mineral magnetic data indicate that there is a difference in the production/preservation of greigite magnetosomes between different basins of the Baltic Sea, which can be connected to the differences in the spatial and temporal distribution of hypoxia/anoxia.

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Many species of MTB are sulphate reducers and others use reduced sulphur compounds to fuel their metabolism (Lefèvre and Bazylinski, 2013). Since there is plenty of iron in the Baltic Sea (Breitbarth et al., 2009) it might be the availability of sulphur compounds (sulphate, sulphide) that limit their growth. On the other hand, the distribution and production of MTB have been suggested to be limited by the prevalent salinity. Martins et al. (2009) showed that the *Candidatus* magnetoglobus multicellularis from the hypersaline Araruama Lagoon, Brazil, dies in salinity > 55‰ and < 40‰. Also, Lin et al. (2012) and (2013) suggest that the MTB distribution is influenced by salinity, among other parameters such as organic matter input (Martins et al., 2012). The existence of greigite producing MTB in the Baltic Sea might be linked to the frequent changes in salinity.

5.3 Magnetosomal Fe fluxes in the Baltic Sea compared to magnetosomal Fe fluxes in other environments

Mineral magnetic evidence of magnetite produced by MTB has been found in Swedish lake sediments (Snowball, 1994; Snowball et al., 1999, 2002). Mineral magnetic properties and varve chronologies are available for three Swedish lakes that have sediment dominated by single-domain crystals with magnetic properties characteristic of magnetosomal magnetite. The data from Furskogstjärnet, Sarsjön and Frängsjön, (Fig. 1) make a comparison possible between the magnetosomal Fe bound as magnetite in lake sediments with the magnetosomal Fe bound as greigite in the Baltic Sea sapropels. The flux of Fe bound as magnetite was calculated with the same method used for the Baltic Sea sediments (Supplement) and is shown in Table 2. Frängsjön and Sarsjön, which are situated in the northern half of Sweden, are significantly different with higher Fe flux in Frängsjön (1.30×10^{-6} g cm^{-2} yr^{-1}) compared to Sarsjön (0.64×10^{-6} g cm^{-2} yr^{-1}). Lake Furskogstjärnet is situated in the middle-west Sweden and has significant higher fluxes of Fe (0.86×10^{-6} g cm^{-2} yr^{-1}) compared to Sarsjön but lower fluxes compared to Frängsjön. The magnetosomal Fe fluxes in the Swedish

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lakes are similar to the magnetosomal Fe fluxes in the Baltic Sea sapropels (0.19–1.46×10^{-6} g cm^{-2} yr^{-1}).

Fluxes of a uniaxial non-interacting single domain (UNISD) ferrimagnetic mineral were calculated for lacustrine sediments in Brownie Lake (Table 2), a small permanently stratified lake in Minneapolis, Minnesota (Lascu et al., 2010). The mineral, produced by MTB, was identified as non-stoichiometric magnetite, with a stoichiometric magnetite core and a non-stoichiometric outer shell of maghemite. Laminated clayey silt (mostly sapropels) in the top 65 cm (65 cm ~ 1850 BP) of the sediment sequence have biogenic magnetite fluxes of $4–12 \times 10^{-6}$ g cm^{-2} yr^{-1} corresponding to a Fe flux of $2.9–8.7 \times 10^{-6}$ g cm^{-2} yr^{-1}. The Fe flux is calculated on the assumption that the mineral grains are stoichiometric magnetite but since they are not, there will be a small error in the calculations. Even so, the Fe fluxes can be compared to the fluxes in the Swedish lakes ($0.6–1.3 \times 10^{-6}$ g cm^{-2} yr^{-1}) and the Baltic Sea ($0.2–1.5 \times 10^{-6}$ g cm^{-2} yr^{-1}). The Fe fluxes from the Brownie Lake are higher than the magnetosomal Fe fluxes in the Swedish lakes and the Baltic Sea, but only significantly (99 % level) higher than the Baltic Sea fluxes. In the Baltic Sea sapropels (greigite) and the studied Swedish varved lake sediments (magnetite) magnetosomes are the dominant ferrimagnetic phase, while the contribution of magnetosomal magnetite in the Brownie Lake is only 1–12 % of the total ferrimagnetic component.

Martins et al. (2009) studied a multicellular MTB (*Candidatus* Magnetoglobus multicellularis) in the hypersaline Araruama Lagoon, Brazil. They estimated the total iron trapped in these MTB to be 7.3×10^{-7} g Fe kg^{-1} sediments, which was negligible compared to the total iron in the Lagoon (2.7 g Fe kg^{-1} sediment), and low compared to the values we obtain for Baltic Sea sapropels ($28–108 \times 10^{-3}$ g Fe kg^{-1} sediments).

Simmons and Edwards (2006) and (2007) used another approach to calculate the flux of Fe bound in MTB in the chemically stratified Salt Pond (north-east coast of USA). They used cell density, Fe content per cell, chemocline width and population turnover time and obtained the estimate that MTB remove Fe at a rate of 2.5×10^{-10} g cm^{-2} yr^{-1}

from the chemocline. In comparison, the Baltic Sea magnetosomal Fe fluxes are 760–4720 times larger.

In this study the contribution of magnetosomal Fe to the biogeochemical cycle of Fe is low, $< 0.7\,\%$, compared to the initial calculations by Simmons and Edwards (2007) where they have values up to $13\,\%$ in the Pettaquamscutt estuary. Although the methods used to calculate the fluxes are fundamentally different, our study shows that the contribution of MTB to the sedimentary pool of iron and sulphur (and oxygen in the case of magnetite magnetosomes) can be highly variable over time and space. The similar maximum values of Fe flux obtained from freshwater and marine sediment sequences points to a common limiting factor for growth and/or preservation, even though they experience quite different geochemical environments. Further research is needed to establish the factors that limit the MTB population dynamics and the abundance of their magnetofossils in geologic media.

6 Conclusions

- Calculated fluxes of Fe (S) bound in magnetosomal greigite in Baltic Sea laminated sapropels ranged between 0.19 and $1.46 \times 10^{-6}\,\mathrm{g\,cm^{-2}\,yr^{-1}}$ (0.15–$1.12 \times 10^{-6}\,\mathrm{g\,cm^{-2}\,yr^{-1}}$), and varied in time and space.

- The magnetosomal Fe contribution to the burial of total and reactive iron is low, only 0.09–$0.19\,\%$ and 0.03–$0.70\,\%$, respectively.

- Fluxes of Fe bound in magnetosomal magnetite in three varved Swedish lakes with organic rich sediments are similar, 0.64–$1.3 \times 10^{-6}\,\mathrm{g\,cm^{-2}\,yr^{-1}}$, to the Baltic Sea magnetosomal Fe fluxes.

- The factors that limit the production and preservation of the MTB magnetosomes are difficult to determine from sediment records because these types of bacteria can adapt to changing environmental conditions, using inorganic and/or organic sources of energy for their metabolism.

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Table 1. Fluxes of magnetosomal iron (Fe) and sulphur (S) to Baltic Sea laminated sapropels of different ages. MWP = Medieval Warm Period, HTM = Holocene Thermal Maximum (for details see the text).

Core	Water depth (m)	Fe flux ($10^{-6}\,\mathrm{g\,cm^{-2}\,yr^{-1}}$)		S flux ($10^{-6}\,\mathrm{g\,cm^{-2}\,yr^{-1}}$)	
		MWP	HTM	MWP	HTM
LZGB2	110.5	0.19	1.11	0.15	0.85
LL19	169.0	0.64	0.45	0.49	0.35
F80	181.0	1.46	0.70	1.12	0.54

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Table 2. Fluxes of iron (Fe) to laminated/varved sediments in comparative sites (see text for details). Fe_R = reactive iron, Fe_T = total iron.

Site	Sediment description	Water depth (m)	Magnetosomal Fe flux bound as magnetite (10^{-6} g cm^{-2} yr^{-1})	Fe_R flux (10^{-4} g cm^{-2} yr^{-1})	Fe_T flux (10^{-4} g cm^{-2} yr^{-1})
Furskogs-tjärnet	lacustrine, varved	14.2	0.86		
Frängsjön	lacustrine, varved	7.1	1.30		
Sarsjön	lacustrine, varved	7.3	0.64		
Brownie Lake	lacustrine, laminated	13	2.9–8.7		
AS5-PC2	brackish, laminated	33		2.2–6.7	
F80	brackish, laminated	181			9–11
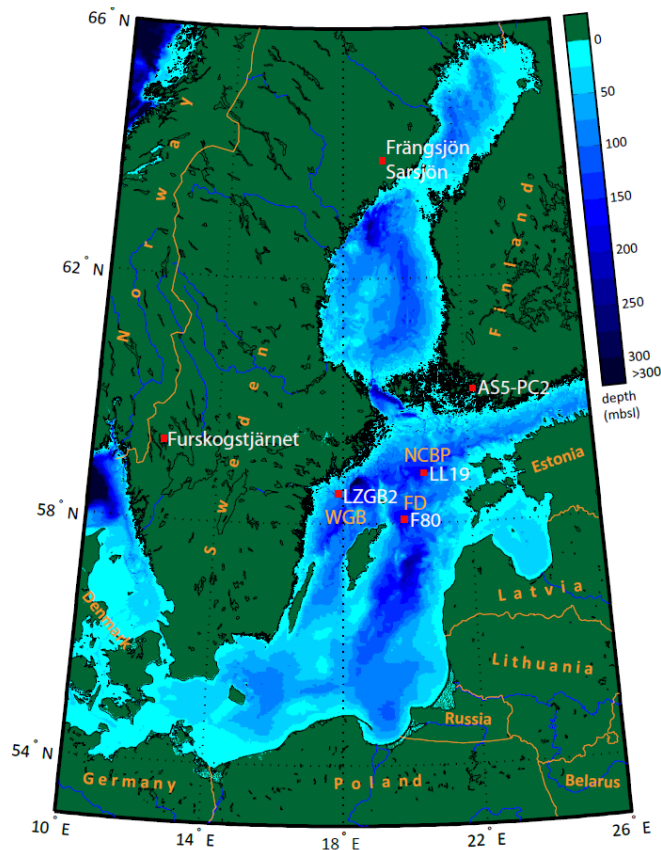
Fig. 1. Positions of coring station LZGB2 in the western Gotland Basin (WGB), LL19 in the north central Baltic Proper (NCBP) and F80 in the Fårö Deep (FD) in the Baltic Sea. Also included are the AS5-PC2 coring station in the Archipelago Sea and the three Swedish lakes; Furskogstjärnet, Sarsjön and Frängsjön. Bathymetric data from IOC et al. (2003).
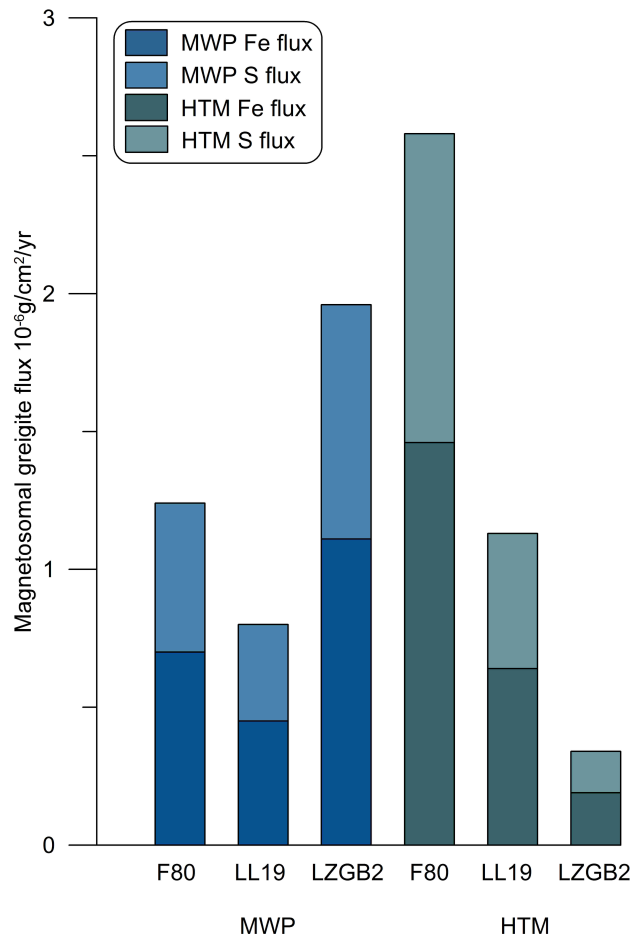
Fig. 2. Magnetosomal greigite, Fe and S fluxes to the MWP and the HTM laminated sapropels for sediment cores F80, LL19 and LZGB2.
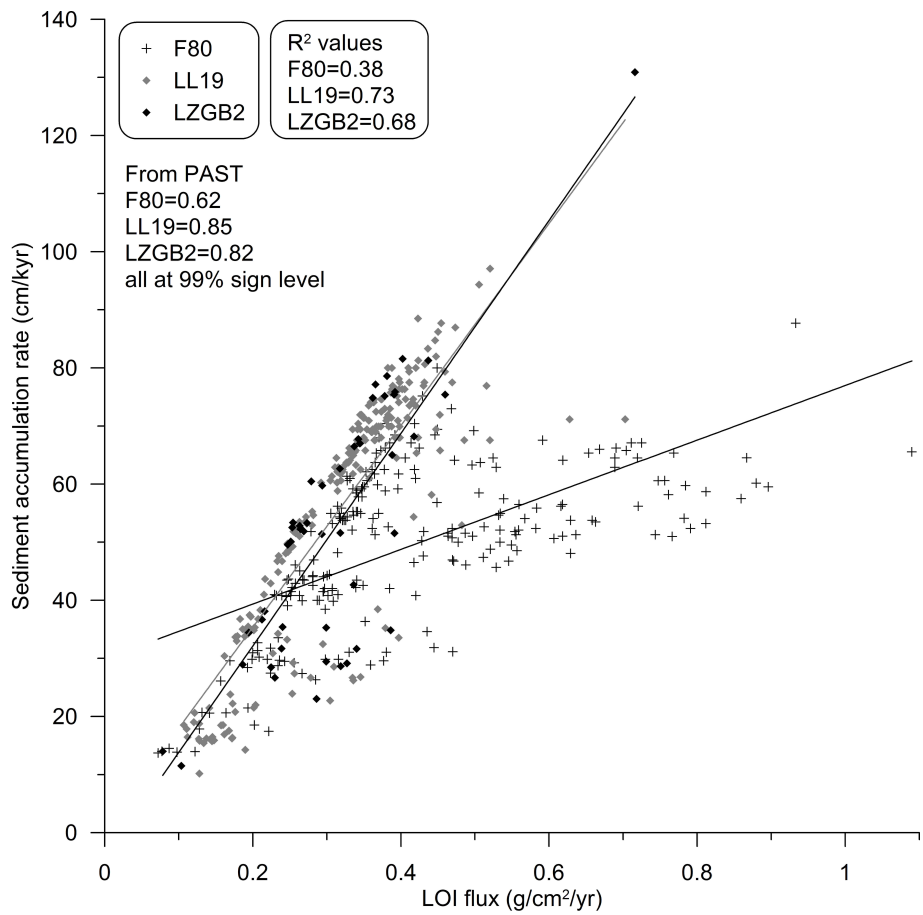
Fig. 3. Sediment accumulation rate vs. LOI flux for sediment core F80, LL19 and LZGB2. The positive correlations are significant at the 99 % significance level.

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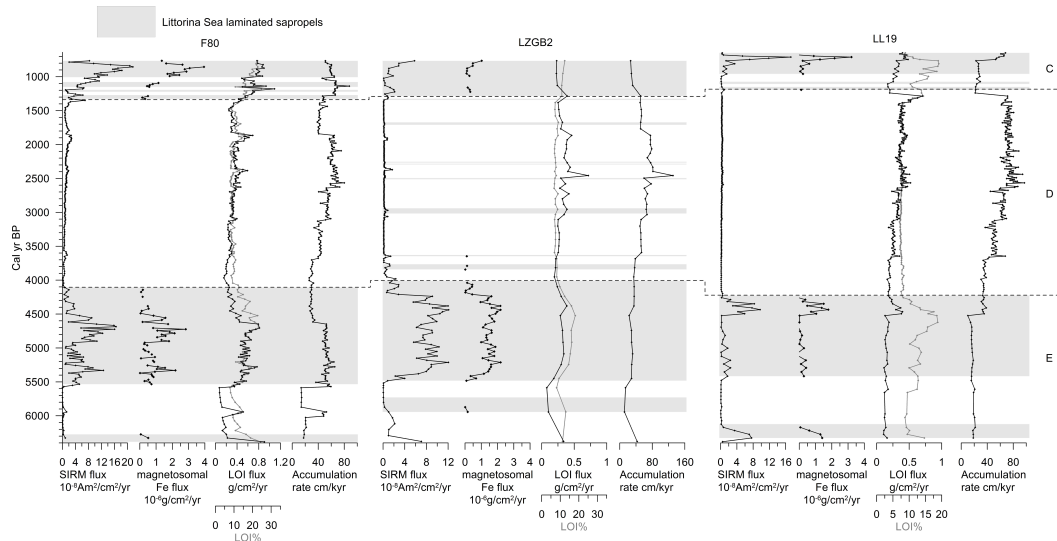Printer-friendly Version

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Fig. 4. Saturation isothermal remanent magnetization (SIRM) fluxes, magnetosomal Fe fluxes, LOI fluxes, LOI %, and sediment accumulation rates at sites F80, LZGB2 and LL19. The sediment units C, D and E identified by Reinholdsson et al. (2013) in F80 and LL19 are found in LZGB2. Units C and E are laminated sapropels while unit D is non-laminated. The fluxes are presented as annual rates.