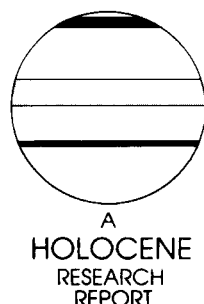# Magnetic investigations of framboidal greigite formation: a record of anthropogenic environmental changes in eutrophic Lake St Moritz, Switzerland

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Abstract: Magnetic minerals found in sediments can either be transported to the basin from the catchment area or can be authigenically formed in the sediments. SEM studies, x-ray diffraction spectra and magnetic mineralogical analyses performed on magnetic extracts from freeze-dried sediments of Lake St Moritz, Switzerland, undoubtedly identified the presence of greigite. The occurrence of this magnetic iron sulphide (Fe_3S_4) is associated with changing environmental conditions that can be interpreted from historical data available for the area. Results of the combined XRD and SEM study show that authigenically formed greigite in Lake St Moritz sediments displays a predominant framboidal crystal arrangement. Amorphous, irregular shapes and spherical aggregates, most often associated with this mineral, are present in lower concentration. These results provide a natural example of framboidal iron sulphide formation and support previous experimental results that have shown that oxidation state and iron availability are critical factors for greigite formation. Despite its metastable character, greigite can also be preserved in the geological record. Its magnetic signature may, in some cases, be representative of a well-defined depositional environment.

Key words: Magnetic minerals, framboidal greigite, iron sulphide, lacustrine sediments, anthropogenic environmental change, St Moritz, Switzerland.

Introduction

Records of palaeomagnetic declination and magnetic susceptibility have been widely used to correlate lake sediment cores. This correlation is usually based on the assumption that magnetic minerals found in lake sediments are derived from the catchment and that they are chemically stable. It has been demonstrated, however, that certain environmental conditions can lead to the formation of authigenic magnetic minerals, such as greigite (Fe_3S_4), in the sediments (Hilton, 1990) as well as to the dissolution of magnetic phases (Anderson and Rippey, 1988). In addition, Mann *et al.* (1990) and Rodgers *et al.* (1990) reported the discovery of several new types of microorganism that precipitate greigite.

Changes in lake productivity brought about by both natural and anthropogenic processes may have an effect on the formation of authigenic magnetic minerals in the lake sediments (Hilton, 1990; Snowball, 1993). However, in order properly to interpret magnetic signals from these lakes as proxy records of productivity and environmental changes, it is important to understand the effects that these changes have on the authigenic formation of magnetic minerals in the lake sediments.

Due to the abundance of detailed historical information available, Swiss lakes provide ideal field sites where annual changes in biological productivity can be monitored, correlated with historical information, and interpreted in the light of linkages between the two. Since the beginning of this century with the increasing anthropogenic impact, the Alpine Lake St Moritz has become eutrophic (Züllig, 1982). As a result of increasing human activities in the catchment area surrounding the lake, major changes in the chemistry of the water column and sediments have occurred in response to an augmented nutrient flux into the system. The eutrophication of the lake since the early 1900s has resulted in the production of organic carbon-rich varves and strong spikes in magnetic susceptibility (Ariztegui, 1993).

Location and characteristics of the lake

Lake St Moritz is a small Alpine lake located in the upper Engadine area of Kanton Graubünden, SE Switzerland. It is the last of a chain that includes the lakes Sils, Silvaplana and Champfer (Figure 1). Situated at an altitude of 1768 m, it has an area of
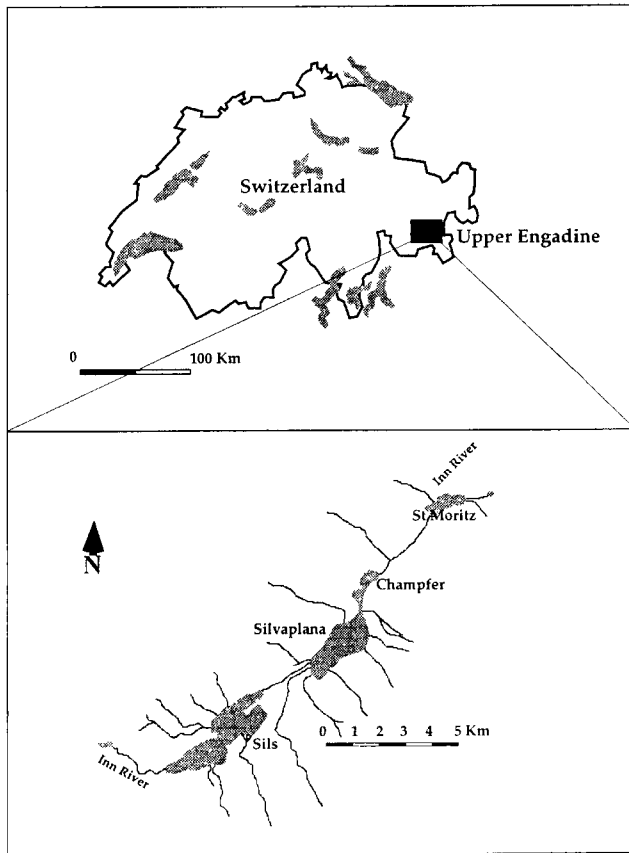
Figure 1 Located in the upper Engadine area, SE Switzerland, Lake St Moritz is part of a chain of lakes: Sils, Silvaplana and Champfer. The Inn River, trending northeastwards, is the main inflow and outflow of the lake.

0.78 km^2, with a maximum length of 1600 m and width of 600 m (Borner, 1922). It has a maximum depth of 44.0 m, averaging 25.0 m, and a volume of 20×10^6 m^3. The average residence time of water in the lake (volume divided by annual outflow) is 0.10 year (Züllig, 1982). The Inn River, trending southwest to northeast, is the main inflow into the lake. Water discharge from Lake St Moritz is also controlled by the Inn River that continues flowing northeastwards.

A high Alpine continental climate dominates the region. It is characterized by warm summers, cold winters, low humidity and plenty of sunshine. Lake St Moritz remains frozen for part of every year, as do most of the lakes in the valley. The climatic features outlined above lead to a typical dimictic response in the Lake St Moritz water column. The break-up of the ice cover starts the annual cycle and produces the spring overturn. The gradual increase in water temperatures promotes the development of a temperature gradient and a well-defined thermocline that reaches a maximum during summer, producing a chemical and physical stabilization of the water column. The thermal stratification breaks up again in autumn, generating the autumn overturn that brings up the nutrients to the epilimnion, while at the same time physically and chemically homogenizing the water column. The development of a new ice cover during winter isolates the system from the atmosphere and produces a winter stratification.

This well-documented annual cycle in the water column is manifested as organic carbon-rich varves in the sediment record. Sedimentological and organic petrographic studies show that each varve couplet comprises a dark, silty lamina, representing increased run-off associated with the spring melt, and a lighter lamina composed of amorphous organic matter and biological remains representing the annual productivity cycle. Occasionally, a third well-differentiated lamina composed of an organic-poor

groundmass mixed with clays occurs, representing the late autumn–winter sedimentation. However, more often, the boundary between the latter two laminae is gradual.

Methods

A gravity-coring device, designed by the Limnology Group of the Geologisches Institut, ETH Zürich, was used to recover a preliminary set of short sediment cores. Long cores were obtained using a coring system based on a modified Kullenberg piston-corer (Kelts *et al.*, 1986). Magnetic susceptibility was measured at a 1.0 cm interval prior to opening the cores, using a Bartington MS2 Magnetic Susceptibility System and an attached MS2C core sensor.

Several methods were used to date the Lake St Moritz sediments: varve counting, ^{137}Cs fallout, historical data and ^{14}C radiocarbon dating. The more recent sediments were dated using the radioactive fallout tracer ^{137}Cs. Its activity was measured in freeze-dried samples from the top 10 cm of the short core; the sampling interval was 1.0 cm. Details of the laboratory procedure and equipment are given elsewhere (Wan *et al.*, 1987). The counting and measuring of annual layers was performed on the core and in photographs.

Magnetic minerals were extracted from some selected core subsamples. The sampling was done immediately after opening the cores, and the material was freeze-dried in order to prevent oxidation. Magnetic extracts were produced by sweeping a cylindrical magnet (200 Gauss in the centre and 750 Gauss on the edges) covered in paper through the dry powder. The separated material (i.e., particles attached to the paper) was suspended in acetone and sonicated, in order to liberate the magnetic minerals from the clay fraction. The magnetic minerals were isolated from the suspension holding the magnet against the base of the beaker; this procedure was repeated several times. The final extract was dried and attached to a greased glass slide for XRD analyses. In order to eliminate the effects of Fe fluorescence, the instrument was equipped with a graphite crystal monochromator.

SEM analyses were also performed on the same samples and magnetic minerals were identified using a Joel JSM 840 SEM coupled with an energy dispersive X-Ray (EDAX) analyzer for element identification.

The magnetic mineral extracts were then set in an epoxy resin capable of withstanding temperatures up to 700°C in order to examine the blocking temperature and coercivity. The samples were given an incremental saturation isothermal remanent magnetization (SIRM) up to 1 Tesla (T), using an Oxford Instruments electromagnet, and the SIRM was measured using an Molspin spinner magnetometer interfaced to a Macintosh SE30. The SIRM was then demagnetized using an alternating field tumbler demagnetizer built at the ETH-Zurich. After AF demagnetization, the samples were given another IRM at 1 T, which was then subjected to stepwise thermal demagnetization in a Schoenstedt oven. In addition, bulk susceptibility was measured during thermal demagnetization with a Bartington MS-2 Magnetic Susceptibility Meter.

For both SIRM acquisition and thermal demagnetization, an epoxy blank of equal volume was measured along with the samples in order to determine the magnetic properties of the resin and to account for its contribution to the remanent magnetization. The SIRM of the blank was two orders of magnitude smaller than the samples containing magnetic extracts, so the contribution of the epoxy to the overall IRM signal should be negligible.

Total carbon, nitrogen and sulphur contents were measured using a Carlo Erba CNS. The analyses were performed on bulk, previously homogenized, freeze-dried sediment samples. Results are reported in weight per cent.

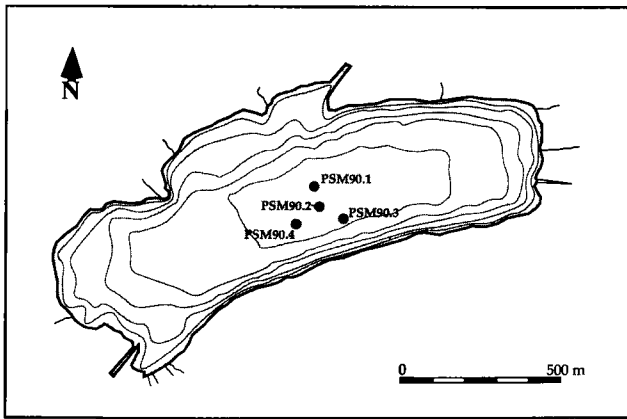The percentage of total organic carbon present in the sediments

Figure 2 Bathymetric map of Lake St Moritz showing the location of the long cores.

was calculated by subtracting the inorganic carbon measured with a Carbon Dioxide Coulometer from the total carbon values obtained from samples analyzed with the Carlo Erba CNS. These values are expressed in weight per cent (% TOC).

Results and discussion

A set of four long cores was taken in the lake (Figure 2). The location of these cores was based on a seismic survey (Ariztegui, 1993). Magnetic susceptibility measurements have been extensively used to correlate lake sediment cores, because they provide a quick and nondestructive method to characterize the sediments (Thompson and Oldfield, 1986). Magnetic susceptibility measurements in Lake St Moritz cores have shown that a similar magnetic response is observed among the different cores. The uppermost section, approximately 55.0 cm in core PSM90.1, is characterized by very low average susceptibilities, and displays three distinctive peaks. These peaks are well defined in all four cores, though PSM90.1 exhibits the strongest peak reaching a maximum value of 20×10^{-5} SI (Figure 3).

The combination of local historical information and varve counting provides an excellent chronology from the beginning of this century. In 1969, preliminary work started in the area to build new ski slopes in anticipation of the '1974 Ski Championship' (Züllig, 1982). This resulted in increased runoff due to deforestation, which is observed as a grey, distinctive *time marker* (Figure 3). This increase in allochthonous input to the sediments carrying detrital magnetic minerals may be responsible for the uppermost two peaks in the magnetic susceptibility record and
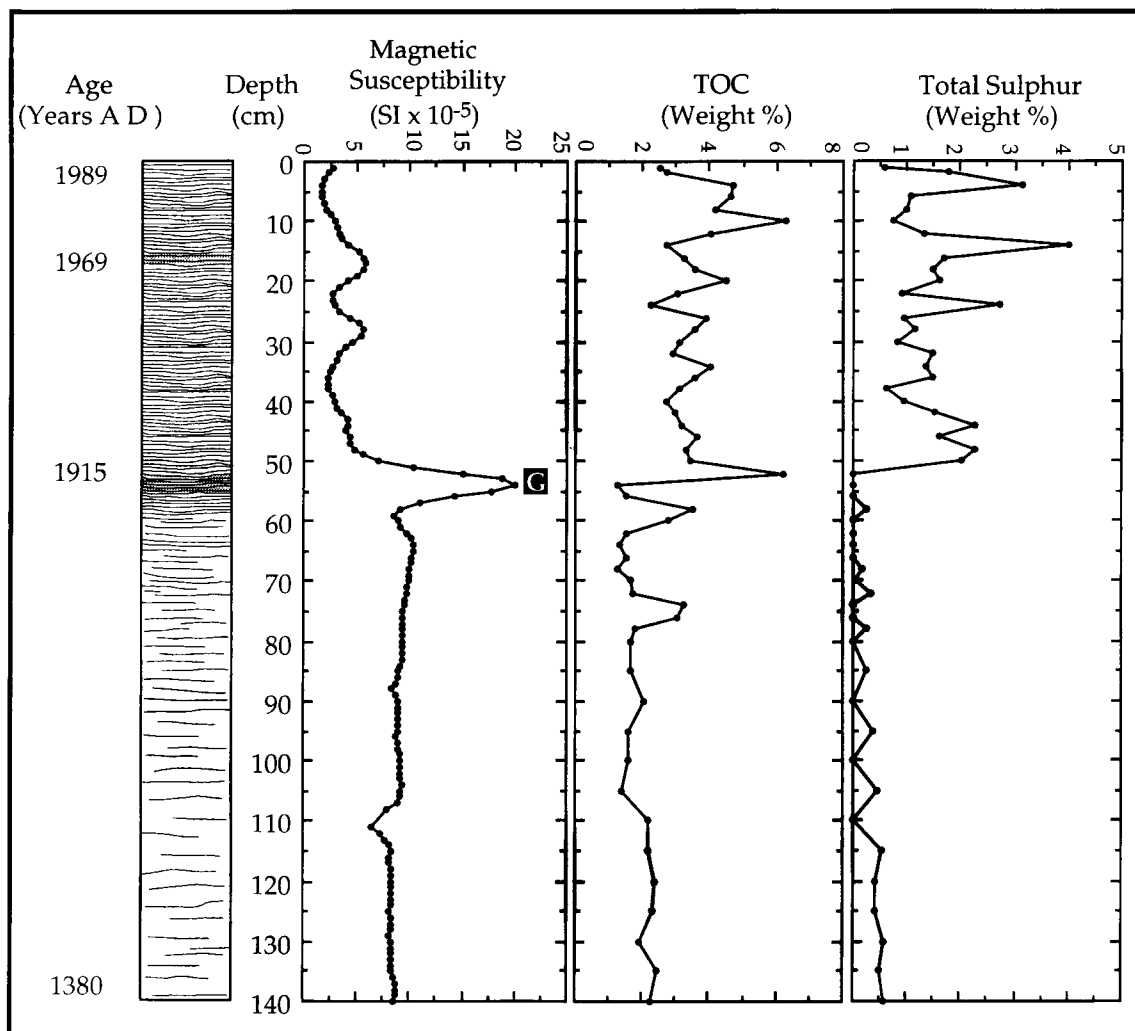

Figure 3 Magnetic susceptibility, total organic carbon and sulphur contents for the uppermost 140 cm of core PSM90.1. Variations in these parameters can be interpreted using a well-established chronology. The magnetic fraction was isolated and concentrated in a selected sample (G) following the methodology outlined in the text.

can be used to correlate different cores throughout the basin. During the summers of 1911 to 1914, a series of dredging operations were carried out on the northwestern shore of the lake. The dredged material was subsequently dumped into the deepest part of the lake and has been recorded in the sediments as a distinctively light grey, massive, clay-rich interval (Borner, 1922).

Figure 3 shows that the sharp change observed in the magnetic susceptibility profile for core PSM90.1 at the beginning of this century – correlated with the dumping of dredged material in the lake – is also clearly marked by the lower values of total organic carbon (%TOC) and total sulphur (%S) observed at this depth. Similarly, the uppermost peaks in the magnetic susceptibility profile correspond with a decrease in both the total organic content and total sulphur percentages.

It has been suggested that environmental conditions are the main factors controlling the sulphur content of sedimentary organic matter (Gransh and Posthuma, 1974). Organic matter concentration, anaerobic conditions and iron-depleted environments are critical prerequisites for the incorporation of sulphur into organic matter in the sediment column. Under anaerobic conditions, if sulphate is available, bacterial sulphate-reduction is promoted and the resulting inorganic sulphur species are able to react with and become incorporated into the organic matter (Kenig and

Huc, 1990). Iron availability in a sulphate-reducing environment leads to the formation of iron sulphides (pyrite, etc.) and consequently to the consumption of inorganic sulphur species preventing its incorporation into the organic matter (Berner, 1984). Chemical and biological data obtained at the time show that the onset of the eutrophication in Lake St Moritz was accompanied by the development of anaerobic conditions in the water column (Borner, 1922).

To determine the nature of the sharp variation observed in the magnetic response, some mineralogical identifications were made. X-ray diffraction analysis (XRD) of bulk sediments showed no evidence of material other than clay minerals, which are usually paramagnetic (small positive magnetic susceptibility). These results are not surprising, as XRD requires a minimum mineral concentration of 5% of the total solid to be registered as a measurable signal. Therefore, it was necessary to extract and concentrate the magnetic fraction of the sample. This fraction was isolated in a selected sample (G in Figure 3) following the methodology outlined in the previous section.

Prior to the XRD analysis of the magnetic extract, it was scanned using SEM in order to determine the morphology of the crystals. Figure 4 shows a series of electron photomicrographs of some of the identified minerals. The two predominant phases were
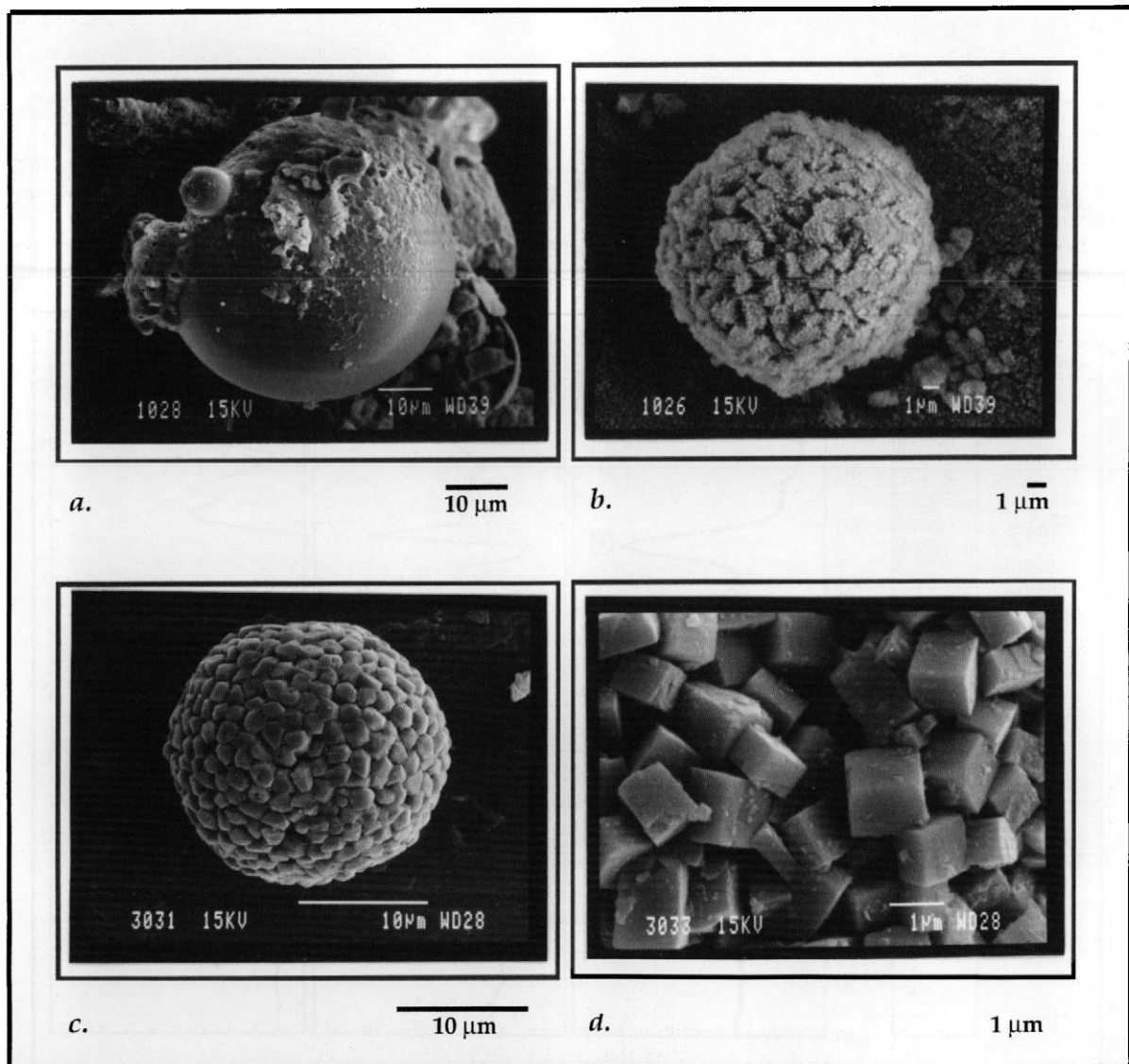

Figure 4 SEM micrographs of some of the iron sulphides identified in the magnetic extract (G in Figure 3). In all cases, the minerals were analyzed with EDAX and, when feasible, x-ray diffraction. The two predominant iron sulphide magnetic phases in sample G display an amorphous (a) and an incipient framboidal texture (b). A better-developed framboidal arrangement of the crystals is observed in micrographs (c) and (d).

analyzed with EDAX (energy-dispersive X-ray analysis). Iron and sulphur peaks were clearly identified, allowing separation from any iron oxides where present, as well as providing an estimate of the relative importance of each. An amorphous, globular phase is observed in micrograph (a). This phase is identical to that observed in laboratory experiments when the initial iron sulphide was transformed to greigite (Sweeney and Kaplan, 1973). An incipient framboidal texture is observed in micrograph (b) while a typical arrangement of the crystals is shown in micrograph (c); a more detailed view is displayed in the micrograph on the bottom right (d). Ferrimagnetic iron-sulphide framboids have been observed in other studies, though the mineralogical species could not be identified (Roberts and Turner, 1993).

XRD analyses were undertaken to verify the chemical composition of the extract. Greigite (Fe_3S_4) can be identified at the appropriate values of 2θ in the diffractogram for sample G shown in Figure 5. The main mineralogical components of the sample are quartz (Q), muscovite (M), chlorite (C) and greigite (G). Peaks at $2\theta \approx 36°$, $30°$ and $25°$ can be separated from the nearby chlorite peaks and are quite diagnostic of greigite. The broadness of the peaks is probably related either to the small particle size and/or poor crystallinity of the minerals. The SEM micrographs indicate that the first factor might play a more important role. Neither magnetite nor hematite have been identified in the sample, although they are the dominant magnetic minerals in many modern lake sediments (Thompson and Oldfield, 1986). Pyrite and marcasite were not identified either.

IRM acquisition and alternating field (AF) demagnetization of IRM indicate the absence of high coercivity minerals (Figure 6). Saturation is reached by approximately 300 mT. Thermal demagnetization of IRM reveals that the majority of the remanence is gone by 350°C. This is consistent with greigite's reported ferrimagnetic ordering temperature of 333°C (Coey, 1988). A sharp decrease in susceptibility is also seen upon heating between 300°C and 350°C. Similar behaviour was observed in the analysis of

freeze-dried magnetic extracts of greigite from Loch Lomond in Scotland, though the decrease in susceptibility occurred between 200°C and 300°C in those samples (Snowball and Thompson, 1988). This may be due to mineralogical changes associated with heating. In addition, a 350°C unblocking phase was seen in thermomagnetic measurements of the Loch Lomond samples.

Conclusions

X-ray diffraction, SEM and magnetic mineralogical analyses indicate the presence of greigite in the Lake St Moritz core. The occurrence of this greigite coincides with a susceptibility peak which is probably representative of changing environmental conditions in the lake.

Previous studies have shown that the formation of greigite requires the presence of an oxidizing agent, e.g., O_2, sulphur, or iron oxides (Goldhaber and Kaplan, 1974). Therefore, its presence in sediments is indicative of well-defined palaeoenvironmental conditions of deposition. This redox status in the water column and sediments can result from the quick injection of oxygen in an anoxic water column, thus producing a geochemical gradient that oxidizes the early authigenically formed iron sulphides leading to the formation of greigite. Sweeney and Kaplan (1973) in a laboratory experiment show that the first iron sulphide precipitated from solution was probably mackinawite. Oxidation of hydrogen sulphide or mackinawite, either by ferric iron or by molecular oxygen, produced elemental sulphur capable of reacting with the mackinawite. Transformation to greigite occurred under these conditions. The organic carbon-rich varves in Lake St Moritz sediments are reflecting not only the onset of the human-induced eutrophication, but also of severe anoxic conditions in both the water column and the sediments. These anoxic sediments overlie more oxic deposits favouring the development of a geochemical gradient. Moreover, dredging operations carried
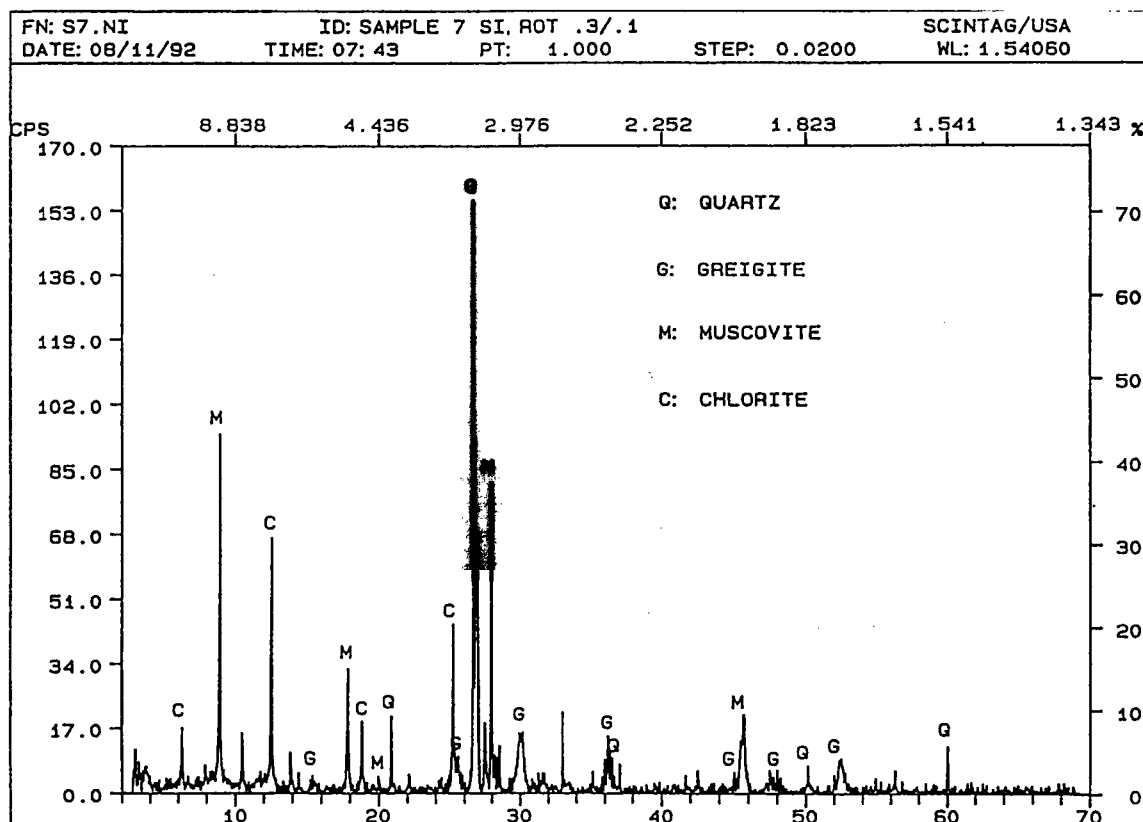

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Figure 5 X-ray diffractogram for sample G. The peaks at $2\theta \approx 36°$, $30°$ and $25°$ can be separated from the nearby chlorite peaks and are quite distinct for greigite.
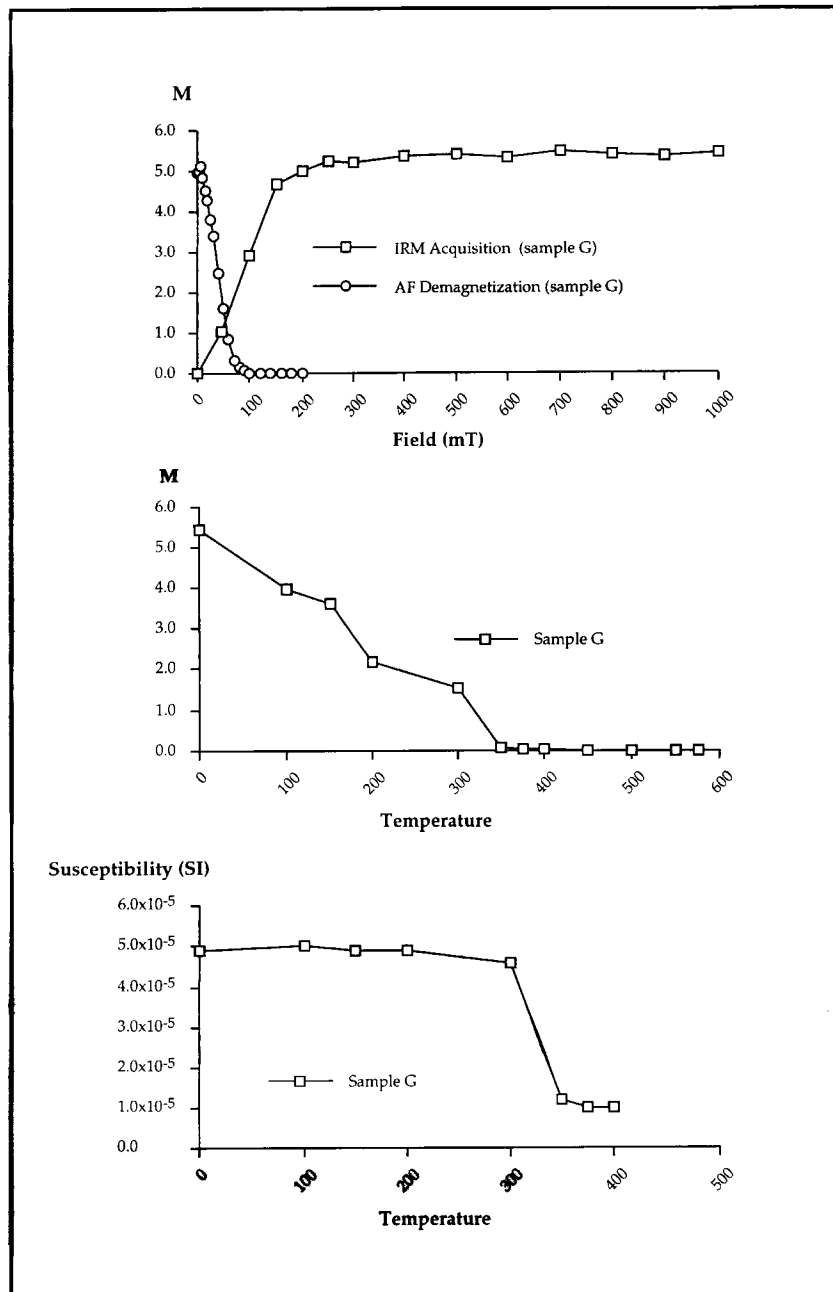
Figure 6 IRM acquisition, thermal and alternating field demagnetization, and bulk susceptibility curves for magnetic extracts from Lake St Moritz. Low coercivity minerals are dominant in the extract according to the IRM acquisition and alternating field (AF) demagnetization of IRM. Thermal demagnetization of IRM shows that most of remanence is gone by 350°C and a sharp decrease in susceptibility is also seen upon heating between 300°C and 350°C.

out in the lake from 1911 to 1914 provided a rapid injection of oxygen in an anoxic water column, as well as an extra source of iron in the lake. These are both critical conditions for triggering the formation of greigite. Experimental studies have demonstrated that the oxidation state plays a critical role in the conversion rate of amorphous FeS to FeS_2 and is probably reflecting a change in sulphur speciation with oxidation state (Schoonen and Barnes, 1991).

Most often greigite appears in irregular, amorphous shapes and spherical aggregates. These suggest it may have formed in association with bacterial activity (Sweeney and Kaplan, 1973). The results of the combined XRD and SEM study presented here have shown that greigite can also have a framboidal crystal arrangement more often associated with pyrite (Sawlowicz, 1993). They provide a natural example illustrating the importance of organic matter in the formation of framboidal iron sulphides.

These results also show that variations in magnetic suscepti-

bility may be due not only to changes in the catchment but also to the formation of authigenic magnetic minerals such as greigite in the lake sediments. Although greigite is metastable, it can be preserved for several million years in sediments as evidenced by its presence in Pliocene marls from southern Switzerland (Freeman *et al.*, 1983). Therefore, its magnetic signature may, in some cases, be used for correlation with environmental events.

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