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71

The occurrence of Greigite in sediments from Loch Lomond

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ABSTRACT: Greigite has been identified in the sediments of Loch Lomond using X-ray diffraction. Greigite is the dominant magnetic mineral in the oldest sediments recovered, while magnetite predominates in the younger sediments which had previously been used for palaeomagnetic secular variation studies. A layer of sediment in between these two magnetic mineral regimes has very low magnetic concentrations, probably as a consequence of magnetite dissolution associated with sulphide rich pore-waters produced at the time of a marine incursion.

The greigite largely oxidises once the sediment is exposed to air, but if freeze dried the greigite becomes surprisingly stable. Following freeze drying the greigite can be heated to 280 °C in air before it alters and loses its strong ferrimagnetic properties.

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KEYWORDS: Greigite, lake, sediments, freeze drying, magnetic susceptibility

Introduction

In the course of a magnetic investigation designed to study sediment core correlations in Llyn Geirionydd, North Wales we observed that magnetic susceptibility was significantly reduced with storage. The concentrations of magnetic minerals in the fresh sediments was very low (very approximately one part in one hundred thousand) and it proved difficult to find any clear way of identifying the magnetic minerals associated with the susceptibility change. Hilton *et al.* (1986) have also observed similar susceptibility changes, involving very low magnetic concentrations, in the surface sediments of Esthwaite Water in the English Lake District. Prompted by these two results we began to investigate a range of Holocene lake sequences and discovered very pronounced susceptibility decreases, over time in Loch Lomond sediments. At this Scottish site the magnetic changes involved much higher magnetic concentrations than those from the English Lake District or from North Wales. This presented us with the opportunity of carrying out more detailed studies of susceptibility loss with storage in lake sediments leading to the identification of the iron sulphide, greigite, as the mineral responsible for the susceptibility change in the Loch Lomond sediments.

In the majority of studies investigating the magnetic properties of lake sediments, magnetite has generally been reported as the dominant magnetic mineral. It normally determines the bulk magnetic properties and is responsible for any natural remanences of the sediments (e.g. Rosenbaum and Larson, 1983; Verosub, 1977). Nevertheless ferrimagnetic iron sulphides, phases of pyrrhotite and greigite have been reported in certain lacustrine sediments by Skinner *et al.* (1964) and Dell (1972).

Susceptibility loss

Subsamples from a six metre core recovered from Llyn Geirionydd in North Wales in 1978 as part of a palaeomagnetic study (Turner, 1980) were selected for susceptibility remeasurement, in the course of a multi-core correlation project. It was discovered that up to 90% of the original susceptibility had been lost over the eight year storage period (Fig. 1a). This prompted the remeasurement of subsamples stored in Edinburgh from a selection of sites. A core from Lake Windermere exhibits a susceptibility loss of approximately 50% over a six year period (Fig. 1b). The concentrations of magnetic minerals in these two cores spanning the Holocene were relatively low (very approximately one part in one hundred thousand) and magnetic extraction techniques were unable to help identify the cause of susceptibility loss. A sediment core collected from Loch Lomond (Scotland) in 1978 using a Mackereth corer (Mackereth, 1958) was subsampled and its magnetic properties measured in 1978 (Turner, 1980). The cubic plastic boxes were subsequently wrapped in wet paper towels, sealed in plastic bags and stored at room temperature. These were unwrapped in 1986 and the susceptibility remeasured. Figure 2a shows a susceptibility loss of up to 5μ S.I. units in the lowermost sediments (some 80% of the original value) and smaller changes

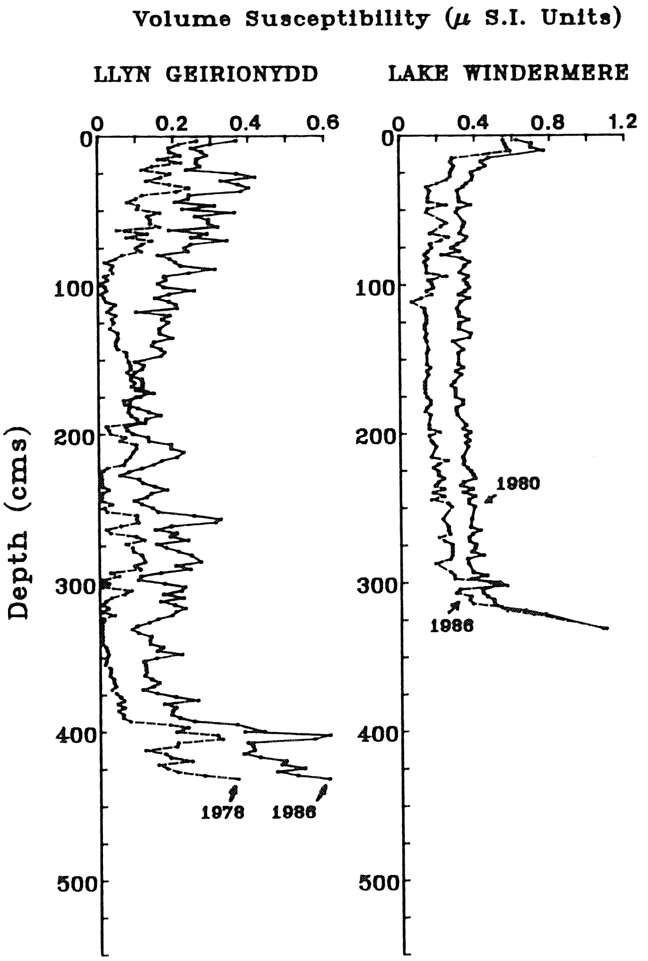


Figure 1 Variation of initial magnetic susceptibility with depth for fresh sediment and stored sediments. (a) Llyn Geirionydd 8 years between measurements; (b) Lake Windermere 6 years between measurements. The Geirionydd sediments show a marked change in χ pattern, notably at 175–200 cm and 300–400 cm. There is a general susceptibility decrease in Windermere sediments of 50%. The lowermost part of the core at 325 cm which does not show a susceptibility decrease penetrated minerogenic material containing little organic matter.

in the more recent sediment. In contrast with the aforementioned sites other lakes containing a full Holocene sequence showed no change in downcore susceptibility patterns, Lake Svinavatn (Iceland) is one example (Fig. 2b).

Identification of magentic minerals

Magnetic extraction

The higher concentration of magnetic minerals in Loch Lomond sediments compared with many of the other lakes studied (shown by a higher volume susceptibility in Fig. 2a) presented the opportunity to extract the minerals in an original way. The zone demonstrating the greatest susceptibility loss was selected for magnetic extraction. Material from an unopened core taken in 1978 was used as no oxidation would have taken place in the sealed core tube. The correct zone was identified by taking a wholecore susceptibility scan (Molyneux and Thompson, 1973) of the unopened core and correlating the results with the subsample measurements from 1978. Material from this zone was freeze dried immediately on opening. Freeze drying provided material in a powdered form, whereas oven-drying in an oxidising environment tends to bake the sediment into solid blocks. A magnetic extract was produced by sweeping a rare earth magnet covered in polythene film through the dry powder. Particles attracted to the magnet were collected and stored in acetone as the magnet was unwrapped. Sediment from Lake Svinavatn, which showed no susceptibility loss during storage, and also had a high magnetic concentration was taken from a freshly opened core and subjected to the same extraction procedure as the Lomond sediment.

The alternative method of pumping material dispersed as a water-based slurry through the poles of a magnet was considered inappropriate. Any authigenic minerals, especially those formed in a reducing environment, would be prone to oxidation and dissolution during the extraction process. Freeze drying appears to alleviate this problem.

X-Ray diffraction analysis

The magnetic extracts were rinsed with acetone, lightly ground and mounted onto glass slides. Powder diffractometer patterns

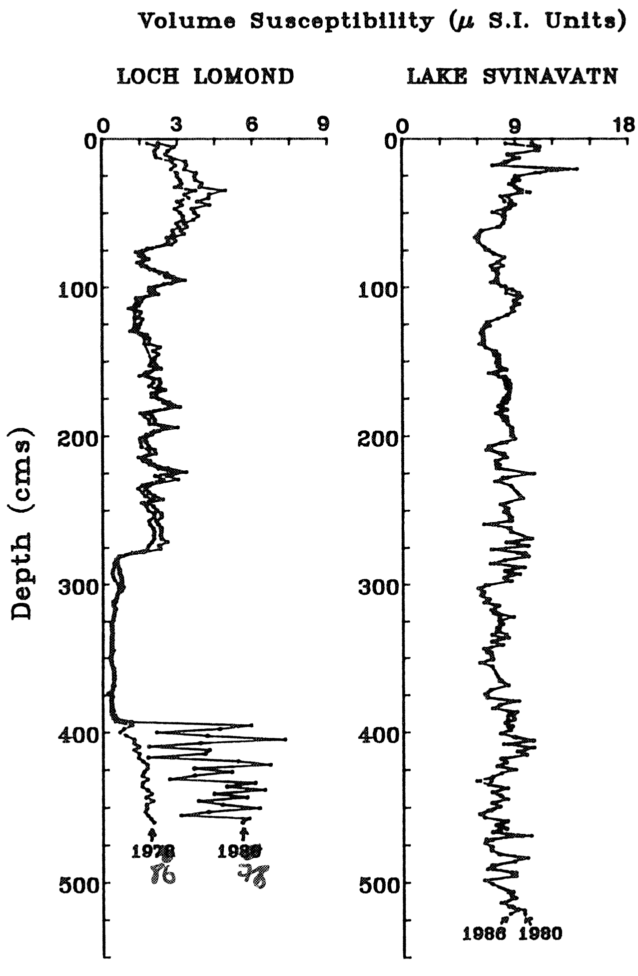


Figure 2 Variation of initial magnetic susceptibility with depth for fresh sediment and stored sediments. (a) Loch Lomond 8 years between measurements; (b) Lake Svinavatn 6 years between measurements. The Lomond sediments show a marked decrease in χ in the lowermost 70 cms, and more minor but still significant decreases in the uppermost 310 cms. No significant changes can be seen in the Svinavatn data.

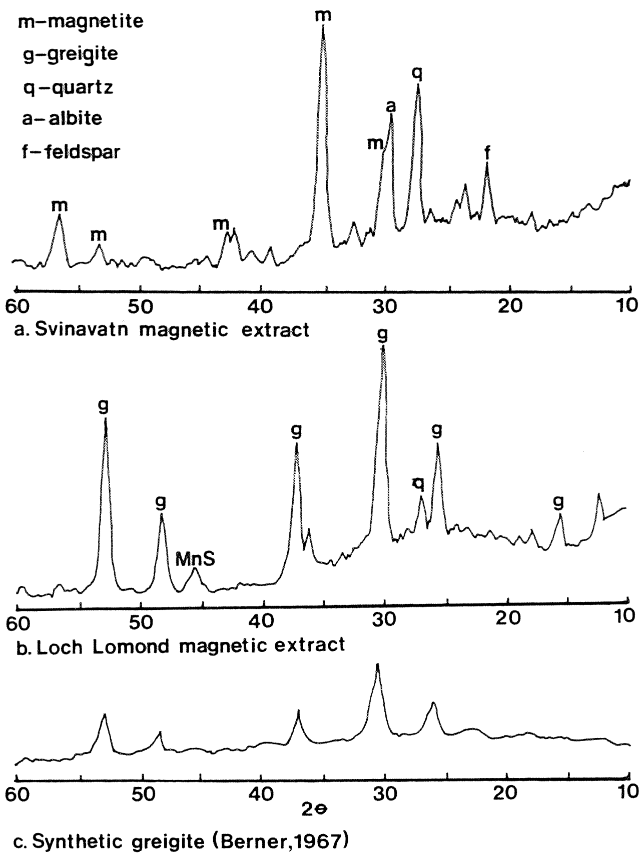


Figure 3 X-ray diffraction patterns. (a) Magnetic extract from Svinavatn sediment; (b) Magnetic extract from Lowermost Loch Lomond sediment; (c) Synthetic Greigite. The Svinavatn extract is mainly magnetite, albite, feldspar and quartz. The Lomond extract is dominated by greigite. Manganese sulphide and chlorite are also detectable.

were obtained on a Phillips PW1010 X-ray diffractometer (Cuα radiation). Figure 3 shows the diffractometer traces for magnetic extracts from Svinavatn (Fig. 3a) and Lomond (Fig. 3b) and for synthetic greigite peaks analysed by Berner (1967). The Lomond sediment clearly reveals six main greigite peaks (labelled g), a low intensity quartz peak (labelled q) and a peak tentatively assigned to MnS. The Svinavatn sediment extract, in contrast, reveals the five main magnetite peaks (m), a quartz peak (q) and a peak probably caused by albite (a).

Thermomagnetic Effects

Magnetic susceptibility and its variation after step heating was investigated for the sediments of Lomond and Svinavatn. Freeze dried bulk sediment was packed into 'pyrex' pots. Their susceptibility was measured at room temperature and after heating and recooling to room temperature at 50 °C intervals to a maximum temperature of 500 °C. The susceptibility of the Lomond sediments decreased on heating to between 200 °C and 300 °C (Fig. 4). The susceptibility of the Svinavatn sediment in contrast slowly increased on heating above 200 °C. This behaviour is typical of sediment containing clay minerals and magnetite; the magnetite remaining stable while the iron rich clays are converted to additional magnetite.

The thermomagnetic properties of greigite have not been well documented on account of the lack of natural samples recovered. Lepp (1957) reported the loss of magnetism of a synthetic iron sulphide (then called melnikovite) at 200 °C. This

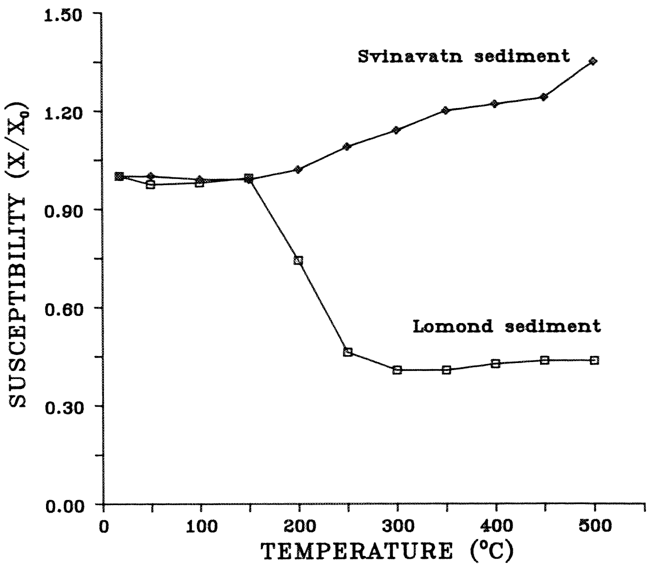


Figure 4 Initial magnetic susceptibility changes following stepwise heating of Loch Lomond sediment and Svinavatn sediment in air. Svinavatn sediment shows the usual heating changes of lake sediment of increasing susceptibility associated with the growth of magnetite by alteration of clay minerals. The Lomond sediment in contrast reveals a drop in susceptibility between 200 °C and 300 °C caused by the alteration of greigite. .

compares well with the step heating results in this study. A magnetic translation balance, designed to measure Curie temperatures, was used to determine the thermomagnetic behaviour of Lomond greigite in a saturation field of 0.5T. The heating curve (Fig. 5) indicates the presence of three decreases in magnetisation at 350 °C, 470 °C and 590°C. The decreases at 350 °C and 470 °C are unknown in the literature and may represent instability temperatures. Their irreversibility is probably dependent upon the atmosphere in which the experiment takes place, as pointed out by Kobayashi and Nomura (1974) in a study of iron sulphides from the Sea of Japan. The latter decrease is probably related to the Curie point of magnetite, formed during the heating process as the sulphides oxidise.

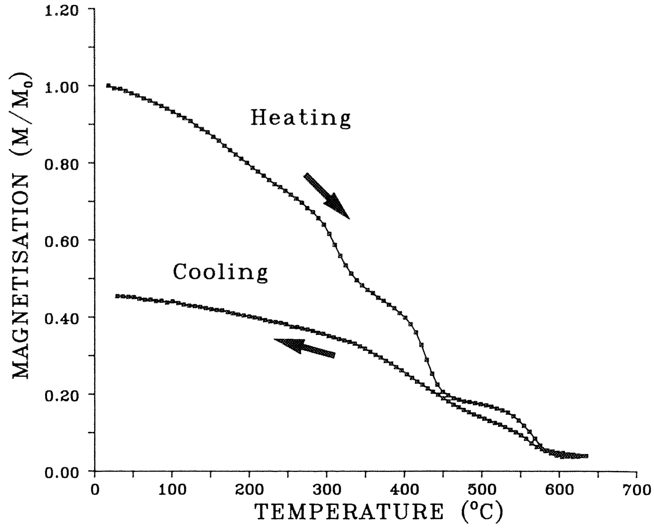
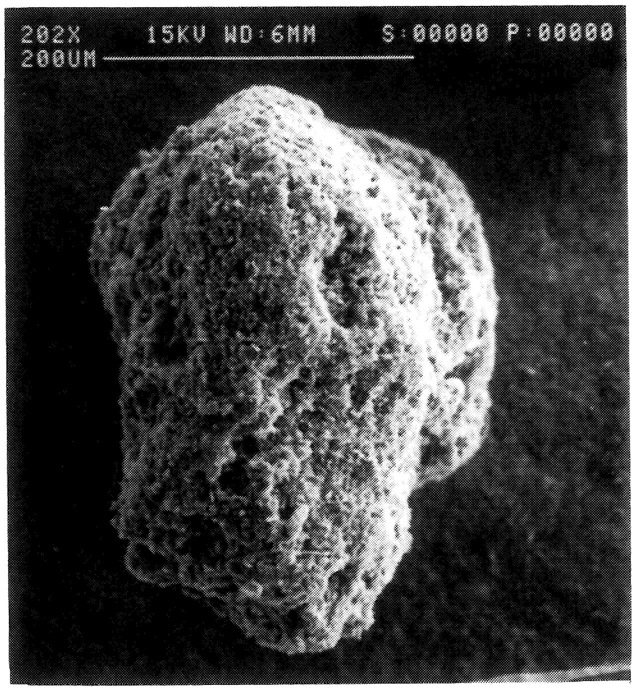


Figure 5 Saturation magnetisation variation with temperature for a greigite extract from Lomond sediment. Curie points or thermal instabilities occur at 350 °C, 470 °C and 590 °C. These are irreversable (see text for explanation).



SEM and microprobe studies

To determine the crystal morphology of the magnetic material, extracts were prepared for viewing under a Scanning Electron Microscope (Cambridge Stereoscan 90). Figure 6a depicts a typical grain of greigite obtained from extraction. Higher magnification (Fig. 6b) reveals a 'platy' structure, individual crystals reaching a size of 5–10 microns in length. This structure contrasts strongly with the cubic greigite examined by Demitrak (1983).

To verify the chemical composition of the extract a quantitative microprobe analysis was undertaken using a Cameca Camevax microbeam. The soft, sooty texture of greigite is not wholly suitable for this technique which requires a hard reflective surface obtained by polishing. However, areas of the larger grains (as in Fig. 6b) with high reflectivity were determined as Fe_3S_4, the expected formula of greigite (Skinner *et al.*, 1964; Berner, 1967). Rarely occurring pyrite particles (FeS_2) were also identified. Stoichiometric pyrrhotite (FeS) was not observed.

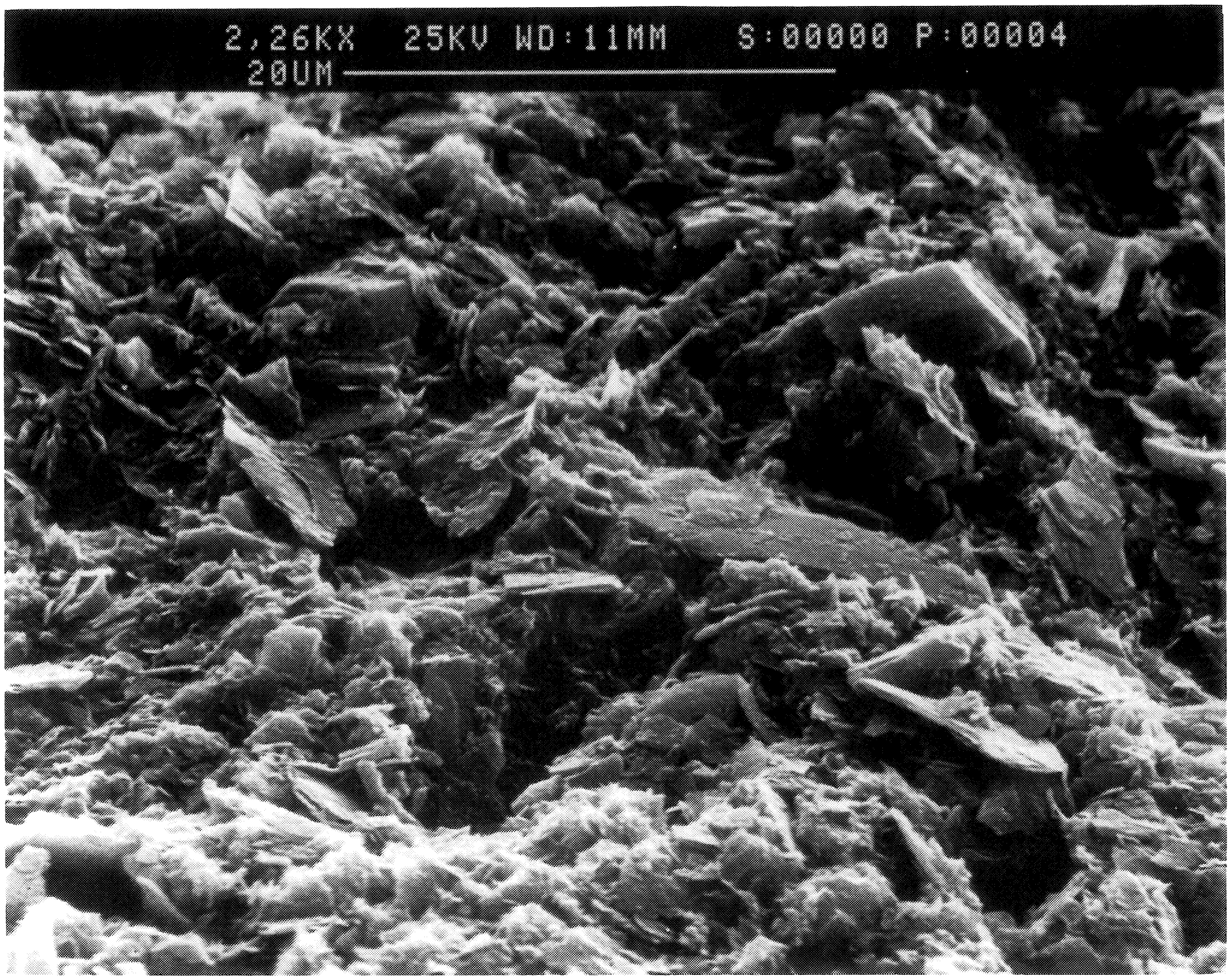


Figure 6 Scanning electron micrograph of magnetic extracts from the Loch Lomond sediment. *Top:* Clump of greigite, horizontal bar is 200 μm; *bottom:* Close up of clump, platy material is greigite. Horizontal bar is 20 μm.

Stratigraphy of Lomond sediments

The stratigraphy of Loch Lomond sediments is complex. A marine incursion occurred during the Late Glacial, causing an inwash of brackish water onto freshwater sediments. The marine transgression is thought to have occurred in the core in Fig. 2a at 390cm and the marine regression at 270cm. The marine sediment between these depths is represented by the 1978 susceptibility minima. The greigite 'rich' zone occurs below the marine sediment where susceptibility rises sharply.

Discussion

The greigite extracted from the lower sediments of Loch Lomond most probably formed authigenically. The high concentration of greigite may be related to the intrusion of seawater onto freshwater sediments and subsequent diffusion of porewater altering the chemical stability of the sediments.

An authentic magnetic mineral, such as greigite, existing in freshwater sediments complicates the post-depositional model of magnetic remanence acquisition, assumed in the majority of palaeomagnetic work. Previous palaeomagnetic results obtained from the Loch Lomond cores (Turner, 1980) can now be interpreted to show that greigite can carry a strong (probably chemical) remanent magnetisation. The extent of the contribution of greigite to the stable remanence remains to be determined.

In addition to the clear greigite-bearing zone of sediment in the lower sediments, the loss of susceptibility on oxidation points to greigite occurrence through the whole of the later Holocene freshwater sequence. The top meter in particular displays this susceptibility drop. Greigite is revealed by X-ray diffraction on magnetic extracts from these upper horizons when prepared by the freeze dried technique but not by the water based pumping method. In the later extracts magnetite is the only magnetic mineral identified by X-ray diffraction.

The occurrence of authigenic magnetic minerals such as greigite in lake sediments can clearly complicate patterns of sediment source relationships based around the erosion, transportation, and deposition of heavy magnetic minerals.

Conclusions

The loss of susceptibility in the lowermost sediments of Loch Lomond can be attributed to the presence of greigite, which oxidises during storage. Greigite is also present in lower concentrations in the upper Holocene sediments, but is only detected when the freeze drying magnetic extraction method is used. The cause of susceptibility loss in the Windermere and Geirionydd sediments has not been positively identified. Greigite may be distinguished from other magnetic minerals by its different magnetic and thermal characteristics in addition to its characteristic X-ray diffraction pattern.

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