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JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 95, NO. B4, PAGES 4471–4479, APRIL 10, 1990

A STABLE CHEMICAL REMANENCE IN HOLOCENE SEDIMENTS

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Abstract. The ferrimagnetic iron sulphide, greigite, has been extracted from freshwater sediments from Loch Lomond and Llyn Geirionydd and identified by X-ray diffraction and thermomagnetic analyses. The authigenic greigite is probably the dominant carrier of a stable natural remanent magnetization in the freshwater sediments underlying marine sediments in Loch Lomond and in the Lateglacial interstadial sediments from Llyn Geirionydd. Mineral magnetic analysis shows that greigite tends to have a higher SIRM/X ratio (approximately 70 kAm^{-1}) than many natural magnetite assemblages. This magnetic characteristic coupled with greigite's ability to oxidize easily and to change to a less magnetic mineral upon exposure to air may be used to indicate its presence in downcore magnetic profiles. Alternating field demagnetization cannot be used to distinguish chemical from detrital remanences in Loch Lomond or Llyn Geirionydd on account of the similar magnetic stabilities of greigite and magnetite. The time lag between the acquisition of the primary detrital remanence and the secondary chemical remanence remains unknown and creates difficulties in understanding the record of paleomagnetic secular variation contained in these lake sediments.

1. Introduction

Magnetic studies of recent sediments are carried out for two distinct purposes. First, geophysicists are interested in investigating recent sediments in order to reconstruct the past behaviour of the geomagnetic field through the natural remanences carried by the sediments. Second, stratigraphers and sedimentologists are interested in the concentration, composition and grain size of magnetic minerals in recent sediments for purposes such as lithostratigraphic core correlation, heavy mineral mapping and iron diagenesis studies.

The magnetic properties of varved clays and organic lake sediments were first studied primarily to try to reconstruct past changes in the geomagnetic field [e.g. Johnson et al., 1948; Ising, 1942; Mackereth, 1971]. For these paleomagnetic studies the magnetic mineralogy of the sediments can help indicate the likely source of any natural remanence carrier. The most common natural remanence carrier in fluvioglacial, marine and lacustrine sediments has been found to be the ferrimagnetic mineral magnetite (Fe_3O_4). The magnetite is commonly thought to be an erosion product, transported by air or water to the deposition site [e.g., Granar, 1958; Haggerty, 1970] and considered to be the carrier of a depositional (DRM) or postdepositional (PDRM) remanent magnetization. Recently, very fine (approximately 0.1 μm diameter), distinctively shaped magnetite crystals, probably of bacterial origin, have been identified as natural remanence carriers in many sediment types [Kirschvink and Chang, 1984]. The other main remanence-bearing minerals found in recent sediments are additional iron oxides (e.g. maghaemite, titanomagnetite, and haematite) the iron-manganese oxyhydroxides and certain iron sulphides. Iron sulphides and oxyhydroxides tend to be associated with in situ chemical change through diagenesis and authigenesis and consequently can be suspected of carrying chemical rather than detrital remanences.

Study of the mineral magnetic properties of recent sediments, as opposed to just the natural remanences, has become of increased interest with the development of portable and sensitive instrumentation for use in rapid nondestructive reconnaissance investigations. These mineral magnetic studies are often efficiently made prior to more definitive, but more time-consuming and destructive, chemical or isotopic work. They often involve examining the acquisition or loss of magnetization following exposure to alternating, pulsed, or direct fields.

During a mineral magnetic study of British lake sediments related to core correlation techniques and sediment influx studies, it was discovered that sediment underlying a marine layer in the Loch Lomond sequence displayed the strange behavior of losing a high proportion of its magnetic susceptibility on drying [Snowball and Thompson, 1988]. Holocene gyttja from Llyn Geirionydd was found to display similar susceptibility losses. The origin of this unusual bulk magnetic behavior was traced to the occurrence of the iron sulphide, greigite (Fe_3S_4). Similar magnetic behavior has been observed by Hilton et al. [1986] in sediments from lakes from northwest England.

The purpose of this paper is to investigate the role of the mineral greigite in carrying a natural remanence of chemical origin in lake sediments in addition to contributing to their bulk magnetic properties.

2. Sediment Sampling and Stratigraphy

2.1 Core Collection

2.1.1. Loch Lomond Four of the Loch Lomond sediment cores used in this study (LLRD1, LLRD2, LLRP5, and LLRP7) were recovered from the southern basin of Loch Lomond using a 6-m Mackereth [1958] corer in 1976 and 1977 as part of a previous paleomagnetic project [Turner, 1979]. Following the discovery of greigite (Fe_3S_4) in these cores [Snowball and Thompson, 1988] a longer 9-m Mackereth corer was used in 1987 to obtain deeper sediments and fresh greigite-bearing material (core LLRP10).

2.1.2 Llyn Geirionydd. Llyn Geirionydd has been extensively cored over the past decade by Edinburgh University. Eight 6-m cores were obtained in 1977 and 1978 for a paleomagnetic project [Turner, 1979] and eleven further 6-m cores were collected in 1985 in order to form the basis for a Holocene mineral magnetic sediment source and deposition study.

The experimental work described below was carried out on sediment cores collected in the mid 1970s and on fresh material collected between 1985 and 1988.

2.2. Sampling and Storage

The mid 1970s cores from both sites were split lengthways into two D-shaped halves. One half of each split

Paper number 89JB03186.
0148-0227/90/89JB-03186$05.00

core was subsampled using plastic cubic holders (6 cm^3) for paleomagnetic measurements, while the other half was sealed in polythene tubing and stored in a cold room. Subsamples taken in 1977, following paleomagnetic directional studies, were wrapped in wet paper towels and sealed in polythene as a method of keepng the sediment wet. As the subsamples taken between 1985 and 1987 were used for mineral magnetic analysis rather than paleomagnetic studies, they were generally dried out at 40°C, following mineral magnetic studies, in order to measure their dry weights.

2.3. Stratigraphy

2.3.1. Loch Lomond. The Loch Lomond stratigraphy exhibits a clear example of a Flandrian marine transgression and regression caused by the interaction of eustatic changes of sea level and isostatic uplift. Early Holocene freshwater sediments are succeeded by marine sediments deposited during the major Scottish marine transgression during which the sea level rose several meters despite continued isostatic uplift. Eventually, the local isostatic uplift overcame the global sea level rise, so that the sea level fell below the local Lomond threshold and freshwater sediments were again deposited in the Loch Lomond Basin, possibly beginning with a period of meromixis [Stewart, 1979].

The contrasting depositional environments of the Loch Lomond sediments are distinguished by geochemical, radiometric, and mineral magnetic results. Iodine and bromine concentrations obtained from neutron activation analysis (NAA) [MacKenzie et al., 1983] are plotted alongside volume susceptibility for core LLRD1 in Fig 1. Here we see how the peaks in iodine and bromine concentration directly reflect marine conditions. Analyses of dinoflagellates through core LLRD1 by Stewart [1979] and Dickson et al. [1978] confirm that this layer of sediment was deposited at a time when Loch Lomond was connected to the Atlantic and contained seawater. Dating by ^{14}C gives calibrated ages of 5450 years B.P. for the top of the marine sediment at 310 cm in core LLRD1 and 6900 years B.P. for the lower transition from freshwater to marine conditions at a depth of 410 cm. Pollen analysis shows that the Elm Decline (5300 years B.P.) occurs at a depth of 307 cm in core LLRD1 [Dickson et al., 1978], which is in good agreement with the ^{14}C age determinations. The distinctive mineral magnetic changes through these freshwater/marine oscillations (Figure 1) allow very quick and precise correlation of the Lomond cores [e.g. Turner, 1979].

2.3.2 Llyn Geirionydd. The Llyn Geirionydd stratigraphy follows the classic British Late Weichselian and Holocene succession. This comprises older Dryas clays, deposited at the time of ice retreat at approximately 13,200 years B.P., followed by organic sediments, of the warmer Late Glacial interstadial until 11,200 years B.P., a return to clays of the younger Dryas cold period and finally the complete Holocene organic sequence beginning at 10,000 years BP. Sedimentation is still continuing today. Older Dryas sediments are found below 545 cm in core G30 (Figure 2). Above these lie organic Late Glacial interstadial sediments (545 to 475 cm). The length of this Late Glacial interstadial zone (70 cm) is unusually long compared with most other Late Glacial interstadial sequences recovered in British lakes. The minerogenic Younger Dryas sediments (475 to 435 cm) are overlain by Holocene sediments. The lithostratigraphic boundaries between these different clay horizons are quite abrupt and distinct (Figure 2) and can be found in several of the Llyn Geirionydd cores. Palynological data [Bloemendal, 1977] and ^{14}C dates [Turner and Thompson, 1981] have been produced for the Holocene sediments in Llyn Geirionydd and provide a good chronology. In particular, the Elm Decline, dated locally at 4755 years B.P., has been identified at a depth of 350 cm in core G2, [Turner, 1979]. This palynological horizon can be correlated to a depth of 400 cm in core G30 using the susceptibility fluctuations of Figure 2.

3. Instrumentation and Laboratory Methods

Initial susceptibility measurements were made using a whole core susceptibility loop [Molyneux and Thompson, 1973]. Subsample susceptibilities measured in 1987 from core LLRP10 were made using a Bartington susceptibility bridge, type M.S.2. A Digico flux gate magnetometer [Molyneux, 1971] was used to measure the remanent magnetic properties of the 6 m core subsamples taken in the mid-1970s. A main frequency alternating field demagnetizer was used to test the stability of the natural remanences. Saturation magnetizations were grown using electromagnets in fields of 1 T and measured on a "Molspin" flux gate magnetometer.

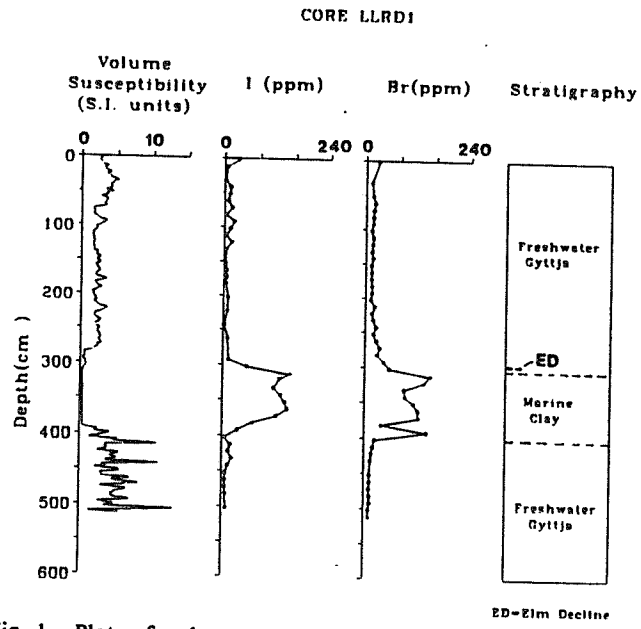

Fig. 1. Plots of volume susceptibility and concentrations of iodine and bromine versus depth, and major stratigraphic horizons for Loch Lomond core LLRD1.

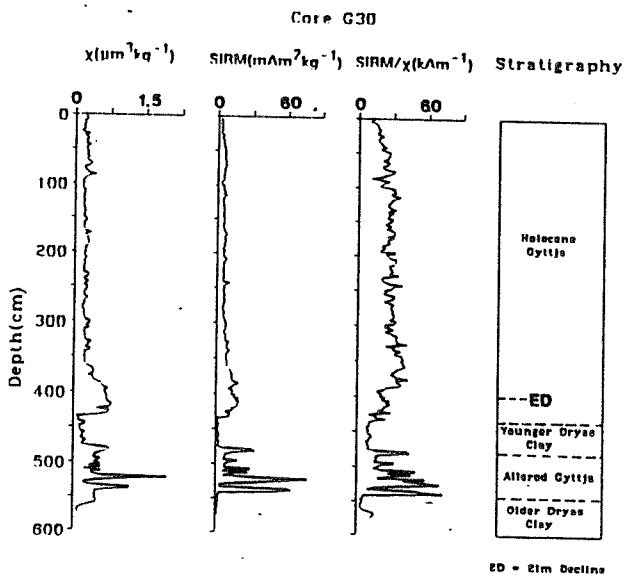

Fig. 2. Plots of susceptibility, SIRM and SIRM/χ ratio versus depth, and major stratigraphic horizons for Llyn Geirionydd core G30.

Special procedures are needed when extracting iron sulphides from wet material in order to prevent their oxidation. Freeze-drying of the sediments has been found to prevent the oxidation of greigite and has been used to prepare sediments for mineral magnetic extraction. Further work has also shown that dispersion of fresh wet sediment in acetone reduces mineral alteration. For this second extraction procedure a magnet covered in a latex sheath is suspended in the dispersed sediment. Material attracted to the magnet can then be rinsed off and stored in acetone.

Thermomagnetic curves of magnetic extracts were obtained using a Curie force balance of a design described by Housden at al. [1988], interfaced to a British Broadcasting Corporation (BBC) microcomputer. A nitrogen atmosphere was provided by designing a thermocouple holder which could also deliver nitrogen from a compressed gas cylinder to the furnace tube. Two reduction valves ensured a constant supply of nitrogen through the furnace. The nitrogen flow rate was minimal. This low flow rate prevented any major force on the samples, as this could affect the magnetization results by moving the samples out of their balance position.

4. Paleomagnetic Studies

Stable single-component remanence directions averaging close to that of the geomagnetic dipole inclination were found in both the Loch Lomond and the Llyn Geirionydd cores collected in the mid 1970s [Turner, 1979; Turner and Thompson, 1979]. Downcore fluctuations in declination and inclination of a few degrees to tens of degrees were documented. The freshwater sediments above the marine layer at Loch Lomond carried an internally consistent paleomagnetic record, and this was interpreted as likely to be of secular variation origin. No signs of dual or multiple magnetic remanence components were detected. Turner [1979, Figure 3.5] noted a difference in the style of the paleomagnetic recording of the natural remanent magnetization of the Loch Lomond sediments below the marine regression horizon. Both the remanent inclinations and declinations of the older sediments were clearly more scattered, so she concentrated on analyzing the paleomagnetic secular variation of the upper freshwater sediments. Similarly, during these mid-1970s paleomagnetic studies more scattered records of declination and inclination of natural remanent magnetisation (NRM) were also observed in the Late Glacial interstadial gyttjas in Llyn Geirionydd [Turner, 1979, Figure 3.15]. Paleomagnetic data obtained from these two sediment types were discarded and not used in the construction of the subsequent United Kingdom secular variation curve. The precise cause of the scattered paleomagnetic intensity and directions was not investigated [G.M.Turner, personal communication, 1987].

Alternating field (af) demagnetizaton of freshly collected material (Figure 3) from core LLRP10 again reveals a paleomagnetic picture similar to that obtained by Turner [1979]. In the greigite-bearing lower layer (which was not analyzed by af demagnetization in the earlier paleomagnetic studies) the natural remanence directions are stable up to peak partial demagnetization alternating fields of 60 mT, showing just one magnetization direction (Figure 3a). The reduction of intensity during demagnetization follows a convex plot, with no inflection in the curve which might point to two natural remanence components of differing magnetic stabilities. Material from the magnetically magnetite-dominated sediment at the top of core LLRP10 shows demagnetization behaviour (Figure 3b) which is identical to that of the greigite-dominated mineralogy at the base.

The paleomagnetic directional data and their demagnetization properties thus give no direct indication that greigite and magnetite may both be natural remanence carriers by revealing either two component magnetizations or different stability components.

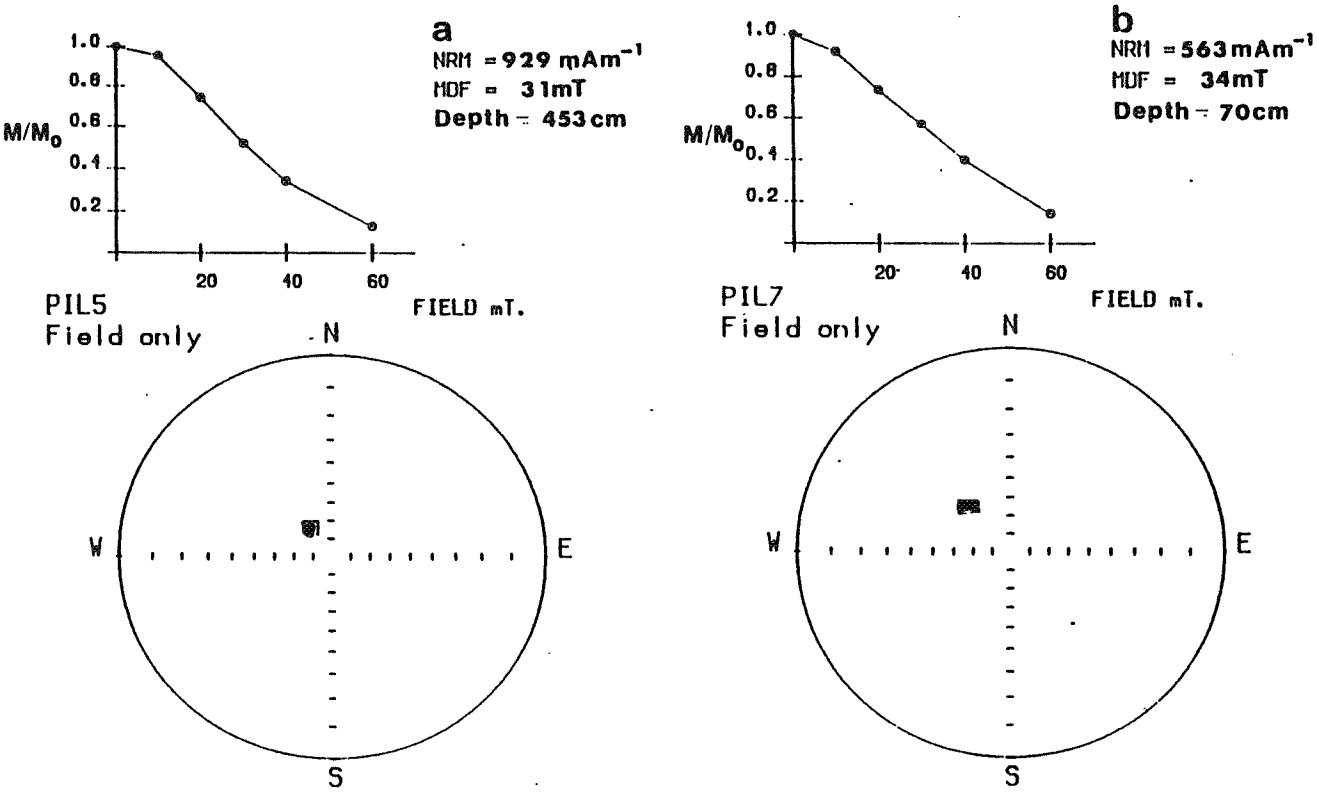

Fig. 3. Alternating field demagnetization results for core LLRP10: (a) greigite-bearing sediment and (b) magnetite bearing sediment.

5. Drying (Oxidation) Experiments

5.1 Core LLRD2

The magnetic susceptibility of subsamples from the bottom meter of core LLRD2 collected in 1977 has been shown to decrease during storage owing to the conversion of greigite to a less strongly magnetic form [Snowball and Thompson, 1988]. Loss of remanent intensity is also found with drying for these sediments. However, this particular decrease in magnetic property is not necessarily a reflection of a drop in magnetic concentration. Such a decrease in remanent intensity on drying may instead be caused by the movement of the magnetic particles as a result of surface tension effects and the realignment of their magnetic moments [Stober and Thompson, 1977]. Alternatively, a decrease in remanent intensity may result from a change in sample shape during drying and storage.

We can, however, investigate the relationship between susceptibility loss and natural remanent intensity using a stratigraphic approach and hence address the question of greigite's being an NRM carrier. The NRM intensity measurements obtained by Turner [1979] for the sediment subsamples from the bottom meter of core LLRD2 are plotted against susceptibility loss between 1977 and subsample remeasurement in 1987 in Figure 4. The positive linear relationship of Figure 4 points to a sediment NRM intensity that is directly related to the concentration of greigite in each subsample in the premarine Lomond sediments.

5.2. Core LLRP5

High values of whole-core susceptibility and whole-core horizontal natural remanent intensity enabled the greigite-bearing zone to be identified in an unextruded mid-1970s core LLRP5. The core was split so that the zone of high remanent intensity could be subsampled. An array of subsamples was taken through the zone of high remanent intensity in order to study the effects of oxidation on the magnetic properties of the sediment. The samples were subjected to a variety of storage treatments in conjunction with repeated magnetic measurements.

Two sets of subsamples were used in a study of saturation isothermal remanence (SIRM) change during storage. One set of subsamples was kept moist and sealed in plastic. The seal around the subsamples was only broken when the samples were required for remeasurement. The second set was exposed to air with the plastic lids taken off. At weekly intervals all the samples were remagnetized in a saturating field of 1 T and their SIRM remeasured.

A very striking contrast in the behaviour of these two subsample sets was found. The sealed subsamples showed no change in their properties (Figure 5). The other subsamples exposed to air however showed a significant decrease in their SIRM. Most of this drop in remanence occurred in the first few days of exposure, when the samples were still moist. After two weeks, when the samples had dried out, no further loss of SIRM was observed.

6. Downcore Magnetic Profiles

The downcore profiles of magnetic susceptibility and SIRM can be interpreted in terms of a changing magnetic mineral composition in both Loch Lomond and Llyn Geirionydd.

6.1. Loch Lomond

Subsample susceptibility and SIRM measurements for the new core (LLRP10) containing 7 m of sediment, are shown in Figure 6. This core penetrates deeper than the 6-m-long cores which were collected from Loch Lomond in the mid-1970s and extends to beneath the greigite-bearing sediment. The layer of marine sediment in this core is once again characterized by low magnetic mineral concentrations. It occurs between 420 and 200 cm and has relatively low susceptibility and SIRM values. The greigite-bearing sediment occurs below the marine horizon between 550 and 420 cm depth. It is marked by high susceptibility and SIRM values (Figure 6). The change in magnetic mineralogy between greigite and magnetite crystals is very clearly reflected in the SIRM/χ ratio which rises to a maximum of

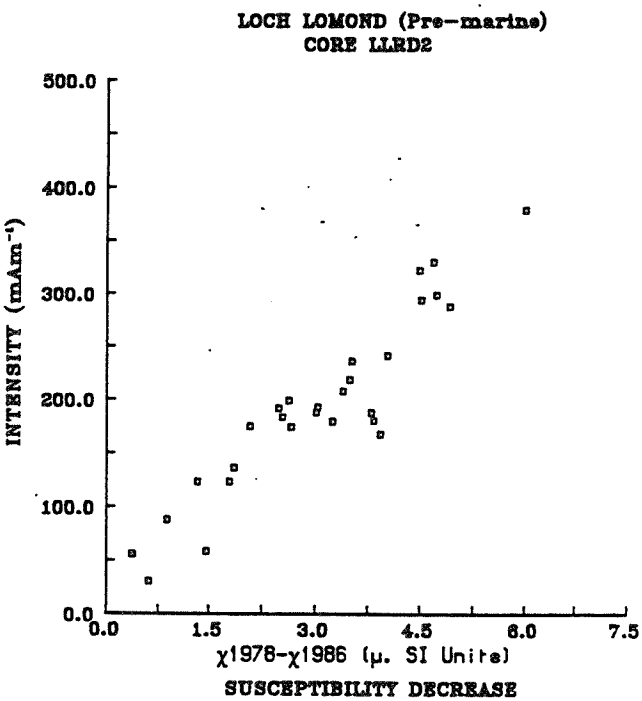

Fig. 4. Magnetic susceptibility loss over a storage period of 8 years versus original NRM for greigite-bearing subsamples from core LLRD2. The strong relationship indicates that the mineral undergoing change during storage is responsible for a large part of the natural remanent properties of the sediment.

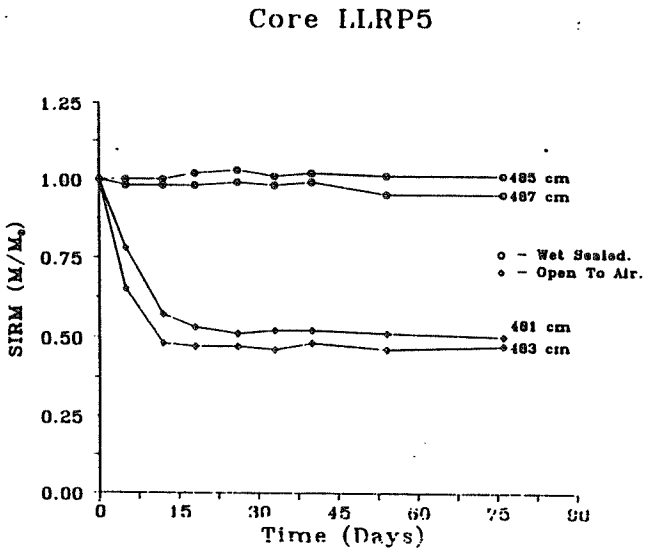

Fig. 5. Time versus SIRM for greigite-bearing subsamples from core LLRP5 stored under different conditions. Note the drop in SIRM when the sediment is exposed to air.

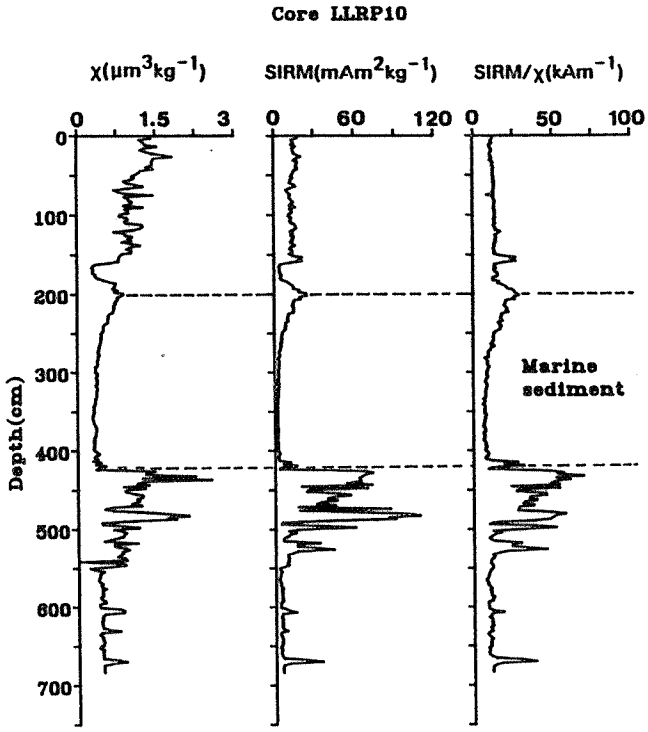

Fig. 6. Plots of magnetic susceptibility, SIRM and SIRM/χ ratio versus depth for core LLRP10.

60 kAm^{-1} in the greigite zone. An average SIRM/χ ratio of 70 kAm^{-1} had previously been obtained for greigite extracted from Loch Lomond sediment. X ray diffraction (XRD) analysis indicated that greigite was the only mineral present in the extracts. Comparison of the SIRM/χ ratios of the high-purity extracts and the new fresh sediment indicates that greigite is probably the dominant magnetic mineral in the sediments immediately underlying the marine zone in core LLRP10.

6.2. Llyn Geirionydd

Two cores from Llyn Geirionydd were selected for identification of the remanence-carrying minerals. The first was core G30 which contains a band of organic sediment (550 to 475 cm) deposited during the Late Glacial interstadial. Figure 2 shows that the Geirionydd Late Glacial interstadial sediment in core G30 has SIRM/χ ratios similar to those of the greigite-bearing sediment in Loch Lomond of above 60 kAm^{-1}. A second core (G36) which also contains a band of sediment with a high SIRM/χ ratio of 100 kAm^{-1} was chosen as well. Sediment from these two zones of high SIRM/χ ratio were used for magnetic extraction and concentration work.

7. Identification of Magnetic Minerals

7.1. Loch Lomond

There is a relatively high concentration of magnetic minerals in the Loch Lomond sediments (around 50 parts per 100,000). This makes it relatively easy to extract the magnetic minerals. Mineral magnetic extracts from the high-concentration zone beneath the Lomond marine layer have X ray diffraction patterns comparable to those of the synthetic greigite produced by Berner [1967]. Additional peaks are caused by minor amounts of quartz and chlorite (Figure 7a). X ray diffraction patterns on extracts from the postmarine sediments of Loch Lomond show a mineralogy dominated by magnetite (Figure 7b).

7.2. Llyn Geirionydd

Concentrations of magnetic minerals in Llyn Geirionydd are rather low (typically 1 part per 100,000). This presents considerable problems for extraction. For example authigenic magnetic minerals present in very low concentrations may be altered and lost during the core extrusion, sampling, and extraction processes. Nevertheless, material extracted from Late Glacial interstadial sediments in core G30 and from the narrow band of high SIRM/χ in core G36 also gave the five main greigite XRD peaks (Figure 7c).

7.3. Scanning Electron Micrscope Analyses

The greigite extracted from Llyn Geirionydd sediments was photographed with a scanning electron microscope (Cambridge Stereoscan 90). The greigite generally occurs in clumps of between 5 and 50 μm in size (Figure 8a) which is smaller than the clumps of up to 200 μm in diameter found

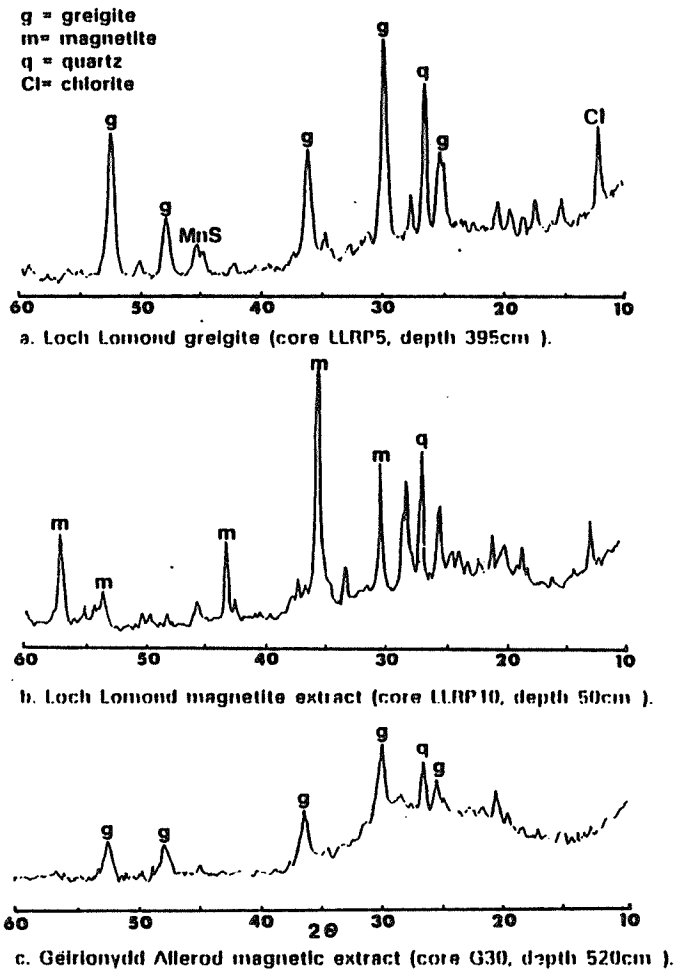

Fig. 7. X ray diffraction patterns obtained for (a) Loch Lomond magnetic extract from core LLRP5 at a depth of 395 cm (greigite is the dominant component along with quartz and manganese sulphide (MnS)), (b) Loch Lomond magnetic extract from core LLRP10 at a depth of 50 cm (magnetite is the dominant component), and (c) Llyn Geirionydd magnetic extract from Late Glacial interstadial sediments (greigite again dominates with some quartz).

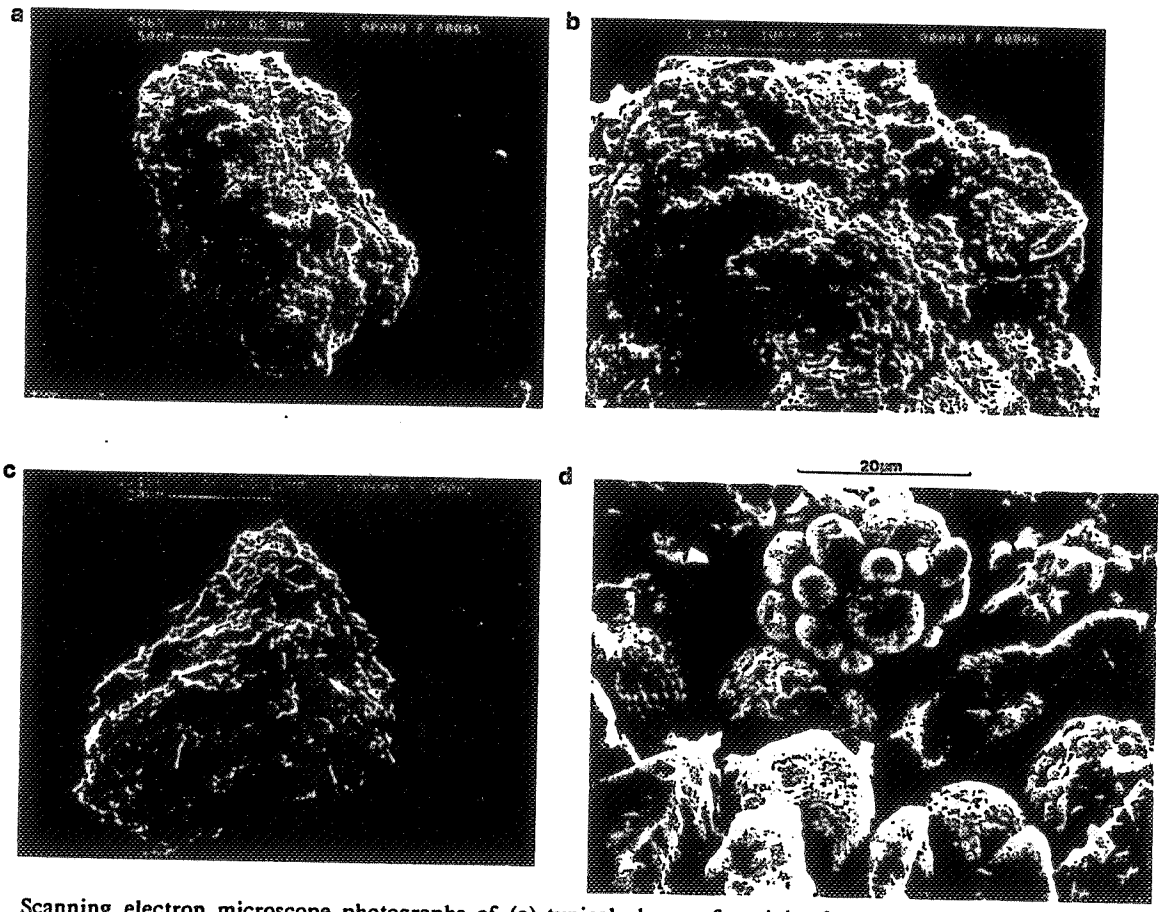

Fig. 8. Scanning electron microscope photographs of (a) typical clump of greigite from Llyn Geirionydd (scale bar is 50 µm), (b) close-up of part of the clump in Figure 8a (scale bar is 20 µm), (c) small clump of greigite from Loch Lomond (scale bar is 20 µm), and (d) a collection of pyrite framboids extracted from marine sediments in Lomond core LLRP10 (scale bar is 20 µm).

in Loch Lomond [Snowball and Thompson, 1988, Figure 6]. Higher magnification (Figure 8b) reveals a poorly crystalline structure. This amorphous form is consistent with the rather broad XRD peaks of Figure 7c.

In Loch Lomond the greigite has a better defined crystal form (Figure 8c) and narrower X ray diffraction peaks than in Llyn Geirionydd. However, at neither site is there any evidence of individual cubic or octahedral grains, which is to be expected of greigite. There have been several reports of naturally occuring greigite, identified with XRD and Mossbauer spectra [Dell, 1972; Skinner et al., 1964; Lepp, 1957], but there is scarce evidence that natural greigite attains its theoretical cubic crystal structure. Demitrak [1985] produced indirect evidence for small cubic greigite particles (<0.1 µm diameter) from Eel Marsh, Massachusetts. However, her particles were not positively identified as greigite.

The magnetic extracts of the marine sediment from Lomond core LLRP10 contain a large number of pyrite framboids, externally similar to the pyrite-coated magnetite grains found by Canfield and Berner [1987 , Figure 3f] in shallow marine materials. A collection of the pyrite framboids extracted from core LLRP10 is shown in Figure 8d. Angular magnetite grains are also present. The pyrite was not present in sufficient concentrations to be identified in the XRD analysis of the bulk sediments but is concentrated by the magnetic extraction process. Attempts were made to investigate the interior chemistry of these framboids by microprobe analysis following the studies of Canfield and Berner [1987] but these were unsuccessful.

8. Thermomagnetic Analysis

Initial studies of the magnetic extracts from the zone of high greigite concentration from Loch Lomond (Figure 9a) revealed the unstable chemical nature of the mineral at elevated temperatures. Rather than a definite Curie temperature marked by a continuing decrease in saturation magnetization on heating, magnetization increases could be found associated with chemical change. Such increases are well known as the result of the production of magnetite from other iron-bearing minerals such as clays during heating in air [Collinson, 1983, p.111]. The non-reversibility of the thermomagnetic curve on cooling could result from the destruction of greigite on heating between 300°C and 400°C. A minor "hump" in the heating curve can be interpreted as resulting from the formation of magnetic iron oxides, possibly a combination of magnetite and haematite. In order to clarify these effects, thermomagnetic analysis was repeated in a nitrogen atmosphere. When the greigite was heated in a nitrogen atmosphere, rather than air, the "hump" in the heating curve disappeared, and the rate of magnetization loss was reduced (Figure 9b). Oxygen obviously aids the destruction of greigite and the formation of new magnetic iron oxides. The greigite is once again irreversibly altered during heating, and no definite Curie temperature can be identified. There is no evidence for magnetite existing in the initial magnetic extracts.

Greigite from Llyn Geirionydd displayed a similar decrease in magnetization during the heating cycle when run in air (Figure 10a). Once again, when the extract was heated

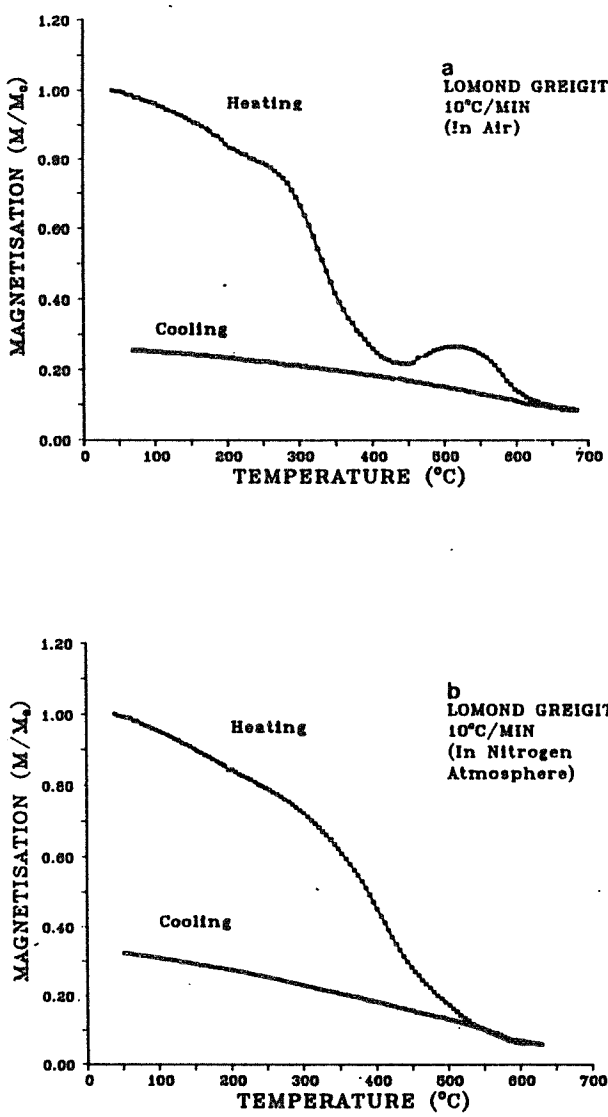

Fig. 9. Thermomagnetic curves for greigite from Loch Lomond sediment obtained using a horizontal force translation balance: (a) heated in air and (b) heated in nitrogen.

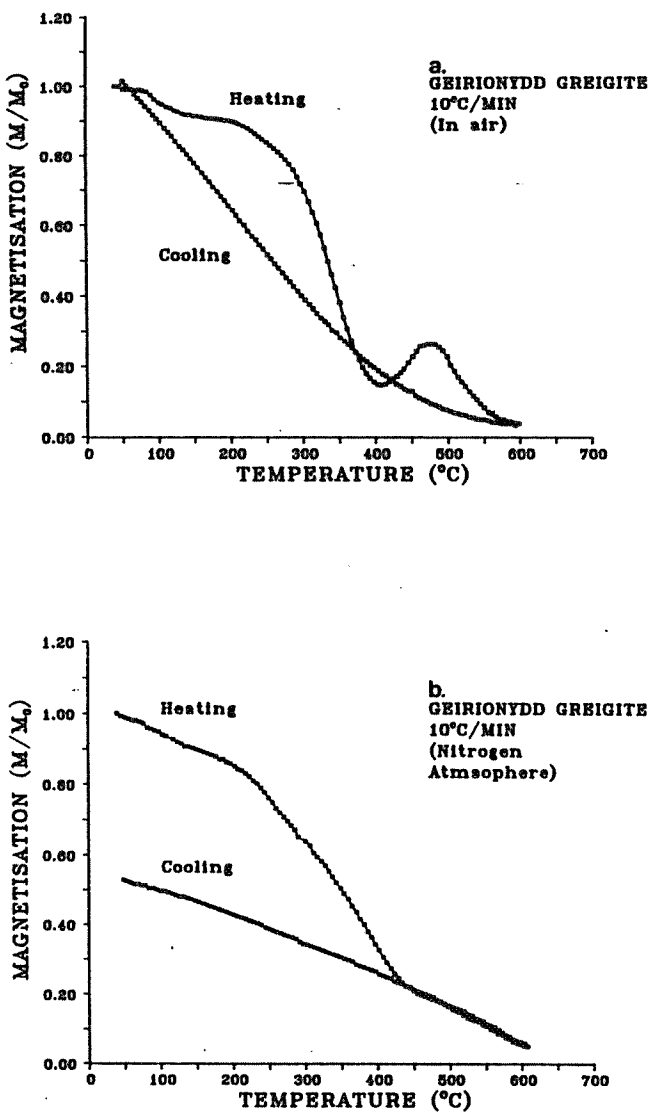

Fig. 10. Thermomagnetic curves for greigite from Llyn Geirionydd, (a) heated in air and (b) heated in nitrogen. Note how in both Figures 9 and 10 the "hump" caused by chemical alteration and growth of magnetic minerals on heating is removed when the experiment is carried out in a nitrogen atmosphere, allowing the thermomagnetic properties of the sulphide phase to be seen more clearly.

in a nitrogen atmosphere no magnetization increases occurred during heating and the rate of magnetization loss was reduced (Figure 10b). The material forming the "hump" when heated in air was irreversibly altered above 500°C. This newly produced material, probably magnetite, appears to be converted to other magnetic iron oxides (e.g., haematite, maghaemite) on further heating, contributing to the rise in magnetization seen on cooling. Minor fluctuations in magnetization up to 200° C are interpreted as being due to the evaporation of acetone, contained within the sample during storage.

Spender et al. [1972] reported an ordering (Curie) temperature of 328°C for synthetic samples of greigite which compares well with the temperature at which the greigite from Llyn Geirionydd and Loch Lomond becomes chemically unstable. There is no evidence in the literature of a reversable thermomagnetic curve for greigite, but rather a temperature range in which greigite becomes unstable. The exact shape of the thermomagnetic curve depends on the heating environment, the rate of heating, the grain size distribution of the greigite, and the purity of the magnetic extract.

9. Discussion

While recognition of greigite in Loch Lomond sediments leads to mineral magnetic interest and application, it unfortunately appears to foreshadow deepening paleomagnetic difficulties.

The distinctive magnetic stratigraphy of the Loch Lomond sediments of Figure 6 can be divided into four zones and accounted for as follows: zone 1 is a lower magnetite-dominated mineralogy which lies beneath zone 2, a greigite-bearing zone of high susceptibility and high SIRM/χ ratio immediately underlying the marine layer (zone 3). The marine sediments are generally of low magnetic mineral concentration and are overlain by a zone 4, a freshwater magnetite zone containing minor amounts of greigite.

Distinguishing between the contributions of magnetite and greigite to the paleomagnetic remanent properties of

these four zones has proved difficult because of the similarities of their magnetic characteristics. The magnetic remanence of the Lomond sediments appears to be carried by greigite immediately below the marine layer (zone 3), but by magnetite in the other horizons. The concentration of greigite, reflected in the downcore magnetic logs of core LLRP10, appears to vary inversely with depth below the marine trangression. We would therefore interpret the high concentration of greigite forming below the marine sequence as a consequence of pore water containing sulphur and sulphides moving progressively as a diffusion-controlled reduction front through the sediment column following the time of the marine transgression when seawater entered the Lomond basin.

The greigite found in Loch Lomond and Llyn Geirionydd is not evenly concentrated thoughout the sediment horizons, which explains the scattered NRM and susceptibility patterns found by Turner [1979] from the analysis of 6-ml sediment subsamples taken from below the marine layer in Loch Lomond and from the Late Glacial interstadial sediments of Llyn Geirionydd. The scattered occurrence of greigite contrasts with the homogeneous distribution of magnetite across synchronous horizons in the upper 3 m of the Loch Lomond cores and the Holocene sediments of Llyn Geirionydd. This difference provides a means by which the magnetite- and greigite-dominated magnetic mineralogies may be distinguished at these two sites. However, mineral magnetic analysis of greigite-bearing Holocene gyttjas from Lough Catherine, Northern Ireland [I.F.Snowball and R.Thompson, unpublished manuscript, 1990], reveals a homogenous distribution of greigite in sediments previously used by Thompson and Edwards [1985] to construct a paleomagnetic record . Therefore a chemical remanent magnetization carried by greigite cannot necessarily be distinguished from a detrital magnetite remanence by the scatter of remanence directions or by an uneven downcore susceptibility pattern.

The close similarities in the stabilities of the two superimposed detrital and chemical remanences create obstacles not only for paleomagnetic directional studies but also for paleointensity work. Normalization methods, using modified Konigsberger ratios or partial, laboratory-imparted anhysteretic remanent magnetizations (ARMs) [King et al., 1983; Levi and Banerjee, 1976], appear quite inadequate for reconstructing paleomagnetic intensities in such sediments. Laboratory experiments using artificially induced remanences and alternating field cleaning do not have the sensitivity to resolve multicomponent remanences in two ferrimagnetic minerals, such as greigite and magnetite, even though the two minerals carry physically quite different natural remanences of distinctive ages.

Dissolution of magnetite in the Lomond marine layer is viewed as occurring through the chemical and magnetic processes set out and skillfully documented by Karlin and Levi [1985] for sediments from the Oregon continental slope. In their studies sulphide pore water reactions contributed to selective dissolution of fine-grained magnetite particles and were found to be responsible for rock magnetic changes, in particular for variations in the viscous remanent magnetization (VRM). These studies have been further elaborated upon by the chemical investigations of Canfield and Berner [1987]. Furthermore the importance of magnetite dissolution in soils with extreme Eh conditions [Duchaufour, 1982, p. 81], particularly in gleyed soil horizons [Maher, 1986], and the likely significance of magnetite dissolution in peat bogs [Williams, 1988] emphasise the likelihood that dissolution effects have a greater bearing on paleomagnetic secular variation studies than hitherto accepted.

Although iron reduction in lacustrine sediments was anticipated by Karlin and Levi [1985], the formation of sulphides which contribute to the magnetic mineralogy was not. The unusually long band of Late Glacial interstadial sediments in Llyn Geirionydd which contain greigite must give rise to concern about the interpretation of paleomagnetic records in freshwater sediments, especially across lithological boundaries where major chemical changes affecting redox potentials may occur.

Marine transgressions and regressions and their resulting sandwich of a marine sediment layer between two freshwater horizons provide cores with very clear geochemical contrasts. In Loch Lomond chemical analyses across the boundaries accurately locate the transgression and regression horizon and in addition document diffusion of sulphur through sediments. As pointed out by MacKenzie et al. [1983], such sediment sequences are important as natural analogues for investigating long-term diffusion effects in clays of interest in connection with low-level radioactive waste storage. The Lomond marine sandwich has also provided us with new information about the origin, stability, and age of magnetic minerals and their paleomagnetic remanences in lake sediments.

Acknowledgments. The authors wish to thank the NERC for financial support, A. Pike for providing reliable coring equipment, and A. Jackson and R. Heath for help in modifying the translation balance. J. Hilton took part in valuable discussions about magnetic minerals in lake sediments. G. Turner and R. Reynolds provided helpful referee comments on the manuscript.

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(Received February 6, 1989;
revised September 13, 1989;
accepted October 9,1989.)