

MÖSSBAUER EFFECT AND MAGNETIC STUDIES OF SECONDARY IRON OXIDES IN SOILS

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Summary

Simple, rapid and non-destructive measurements of magnetic properties (magnetic susceptibility, saturation isothermal remanent magnetization and coercivity of isothermal remanence) coupled with more time consuming and sophisticated analyses such as thermomagnetic and Mössbauer effect studies, provide a basis for identifying forms of iron oxide present in the soil.

At two of the sites studied, Caldy Hill, Merseyside, and Llyn Bychan, N. Wales, the secondary ferrimagnetic oxide formed in surface soil as a result of recent forest fires is shown to be non-stoichiometric magnetite approximating to the formula $\text{Fe}_{2.9}\text{O}_4$. No evidence for the presence of maghemite was found in any of the soil samples from these sites or in soils from the Annecy region of S.E. France.

Introduction

NUMEROUS studies record the formation of secondary ferrimagnetic iron oxides in soils developed on sedimentary rocks. In a recent review article, Mullins (1977) summarises evidence for the origin, nature and composition of the oxides so formed and concludes that several possible mechanisms are involved, including burning, dehydration of lepidocrocite, and the alternate wetting and drying normally involved in pedogenesis. He cites several authors who have used a variety of techniques to identify the ferrimagnetic minerals in soils but recommends caution in evaluating the conclusions reached (p. 234). Although Neumeister and Peschel (1968), and Vadyunina and Kovtun (1974) claim to have identified magnetite, the majority of authors, whether on the basis of experimental methods designed to simulate the pedogenic processes inferred (e.g. Tite and Mullins, 1971, Taylor and Schwertmann, 1974), X-Ray diffraction studies or, more recently, Mössbauer effect studies (Longworth and Tite, 1977), have followed Le Borgne (1955, 1960) in identifying the mineral resulting from enhancement by thermal and/or chemical transformation as maghemite.

Recent studies of magnetic minerals in lake sediments suggest that they provide not only a rapid means of core and sample correlation but also a powerful tool in differentiating types and sources of allochthonous input (Thompson *et al.*, 1975; Oldfield *et al.*, 1978). Evaluating and interpreting the contribution to lake sediments of secondary magnetic minerals formed in the soil depends in part on a further understanding of their origin, nature and chemical composition as well as their persistence, in the soil itself, during transport and in the depositional environment of the lake.

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Materials and extraction methods

Soils used in the present study come from three areas. Caldy Hill, Merseyside (Grid. Ref. SJ223858) in N. England forms part of an outcrop of Triassic (Keuper) Sandstone bordering the Dee Estuary. Heather, gorse and bracken heathland has developed over the bedrock with very little trace of a soil profile save for shallow accumulations of litter and raw humus. Llyn Bychan (Grid. Ref. SH752593), a small lake lying at 250 m in the Gwydyr forest area of N. Wales, is surrounded by shallow peats, peaty podsoles and outcrops of locally mineralized Ordovician Slates. Both the above sites have been subjected to extensive burning since July 1975 and have yielded samples used in the magnetic and Mössbauer effect studies. The soils of the Annecy region of Haute Savoie in E. France are mostly developed on Jurassic limestones and shales sometimes mantled by glacial drift derived in part from areas of igneous and metamorphic rock to the south east.

In several cases, extracts were prepared in order to concentrate the magnetic fraction for subsequent tests. The method used was to suspend the disaggregated soil in water. The suspension was then poured into the top of a vertical Emery tube, an open cylinder 1 m long with a constriction at the lower end into which a tap is set to regulate the rate of flow. By clamping a strong horseshoe magnet close to the base of the tube it is possible to collect magnetic material adhering to the inner walls of the tube in the high field gradients adjacent to the magnet. This material was subsequently flushed into dishes, dried and retained for measurement. In the case of the Caldy Hill (1975 burn) and Annecy (G/3/1 and M/13/2) soils, the magnetic extracts and the non-magnetic residues retained after extraction were used for thermomagnetic study. Mössbauer effect studies were carried out both on magnetic extracts and on bulk samples (Fig. 7) though the data presented refer mainly to the magnetic extracts (Figs 8–11). The Annecy soil submitted for Mössbauer measurement had a significantly lower susceptibility than did those used for thermomagnetic study.

*Magnetic susceptibility and isothermal remanent**Magnetization studies*

Magnetic susceptibility (χ) was measured using the methods outlined in Molyneux and Thompson (1973) and Oldfield *et al.* (in press). All measurements quoted are specific susceptibilities. Saturation Isothermal Remanent Magnetization (IRM_{sat} , SIRM or I_{RS}) was determined by placing oriented samples in a field of 1 T for a few seconds and measuring the magnetic remanence induced, using a slow speed spinner magnetometer (Molyneux, 1971). Figures quoted are for specific I_{RS} . Coercivity of saturation Isothermal Remanent Magnetization (B_{CR}) (the back field required to reduce the IRM to zero) was determined by placing the same samples in successively higher reversed fields from 0.01 T upwards (*cf.* Oldfield *et al.*, 1978).

These parameters permit preliminary identification of the magnetic minerals present in the soil since they help to differentiate ferrimagnetic from antiferromagnetic behaviour. Ferrimagnetism results from a strong A–B spin interaction between the sub-lattices in spinel structure iron oxides and occurs when the sub-lattice magnetizations are opposite but unequal. It is exhibited by magnetites and maghemites and is characterized by high specific susceptibility, saturation magnetization and saturation remanence. The coercivity of remanence in natural ferrimagnets is commonly about 0.02 to 0.04 T. In contrast haematites carry a canted antiferromagnetic remanence. Their sub-lattice magnetizations are not exact-

ly antiparallel and a small net magnetization occurs. The haematites thus have lower susceptibilities, remanences and magnetizations but extremely high coercivities. The high coercivity is due to the crystalline structure rather than shape of the grains and for all but the largest natural grains exceeds 0.2T.

Caldy Hill

In August 1975, a heath fire burned a small area from which samples of parent material and recently burnt and unburnt surface soil (0–2 cm) were taken for study about 2 weeks later. The bulk samples and the silt plus clay fraction from these form the basis for most of the magnetic measurements from the site. A second fire on identical parent material less than 200 m distant, during August 1976, provided burnt surface soil for Mössbauer studies.

Table 1 summarizes susceptibility measurements from bedrock and soils at the site. Unaltered bedrock gives values of $\sim 6 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$, the bulk soil samples, values between 9 and $21 \times 10^{-7} \text{ m}^3 \text{ kg}^{-1}$ with the higher figures associated both in 1975 and 1976 with recent burning. Dry sieving into the three size fractions shows that in both the recently burnt and the unburnt soil, highest specific susceptibility values are in the $<63 \mu\text{m}$ size fraction with the peak value, $4.3 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$, within the burnt soil. Removal of organic matter from this sample by flotation permits recalculation of a specific susceptibility of $5.8 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$ expressed on the basis of inorganic dry weight. In summary, magnetic enhancement by 1–2 orders of magnitude is indicated by the figures quoted, and burning may be inferred as the dominant mechanism involved since the whole area is subject to frequent localized fires.

Fig. 1 compares B_{cR} profiles for nearby bedrock, for the $<63 \mu\text{m}$ fraction from the 1975 burnt material and for a sample of parent material taken from a partially weathered rock face close to the edge of the burnt area. Unweathered bedrock has a coercivity spectrum which indicates the virtual absence of ferrimagnetic iron oxides and a complete dominance of the magnetic minerals by fine-grained antiferromagnetic haematite. The other two samples show a rapid change of IRM in fields up to

TABLE 1
*Magnetic susceptibility measurements of soil and
bedrock from Caldy Hill*

	$\times (10^{-8} \text{ m}^3 \text{ kg}^{-1})$
Local Triassic Sandstone	6
1975 Soil from unburnt area	
Bulk sample	90
$>2 \text{ mm}$ fraction	9
$63 \mu\text{m}$ – 2 mm fraction	65
$<63 \mu\text{m}$ fraction	190
1975 Soil from recently burnt area	
Bulk sample	170
$>2 \text{ mm}$ fraction	50
$63 \mu\text{m}$ – 2 mm fraction	70
$<63 \mu\text{m}$ fraction	430
$<63 \mu\text{m}$ fraction/inorganic matter	580
1976 Soil from recently burnt area	
Bulk sample	210

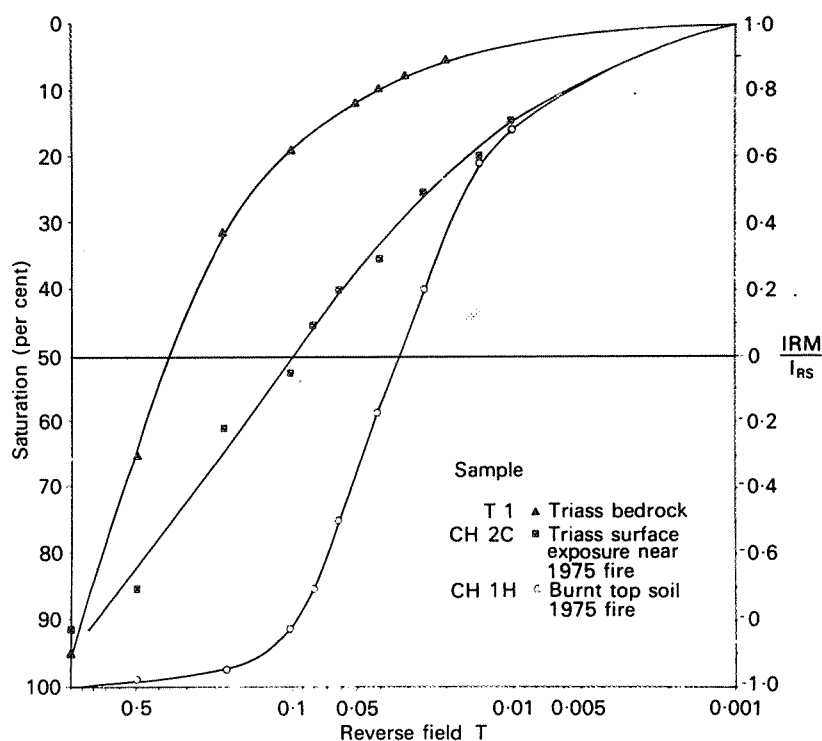


FIG. 1. Caldy Hill. Coercitivity of IRM (B_{cR}) profiles for unweathered bedrock (T1), and for the finest particle size fraction ($<63 \mu\text{m}$) taken from a partially weathered rock face close to the edge of the burnt area (CH2C) and from burnt topsoil (CH1H).

0.02T pointing to the presence of ferrimagnetic oxides. In higher reversed fields the spectra diverge in a manner consistent with dominance of the burnt soil extract by fine grained ferrimagnetic magnetite/maghemite and the parent material by fine grained antiferromagnetic haematite. The failure of the soil extract to saturate in a reversed field of 0.1T probably indicates the survival of a significant amount of haematite in the soil sample (*cf.* Table 3), though proportionally much less than exists in the parent material. The susceptibility data and the B_{cR} profiles may be interpreted as reflecting the partial transformation of antiferromagnetic haematite cement within the parent material into ferrimagnetic iron oxides largely if not entirely as a result of burning.

Llyn Bychan

A substantial part of the lake's catchment was burnt in a major fire during August 1976. This provided an opportunity to study the nature of the magnetic minerals formed during the fire, their persistence in the soils and their incorporation into stream and lake sediments. Over thirty samples were taken from soils in the burnt and unburnt parts of the catchment in addition to several from stream bedloads as well as cores from the lake sediments.

Specific susceptibilities for parent material derived from local mining waste, from the base of soil profiles and from the bed-load of streams draining unburnt

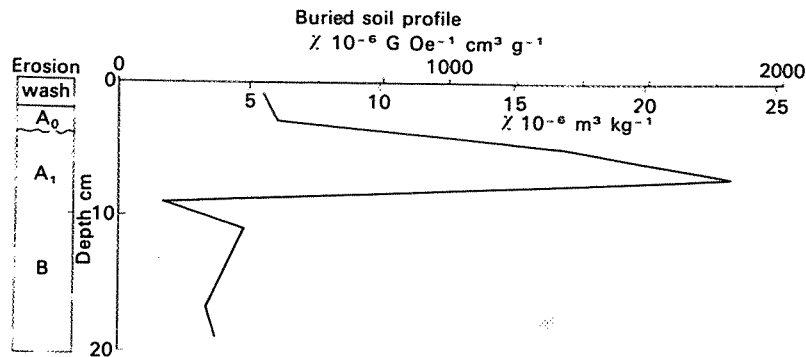


FIG. 2. Llyn Bychan catchment. I_{RS} values from a burnt and subsequently buried soil profile; fire occurred in August 1976; the samples were taken in December 1976.

areas ranges from 7.5 to $90 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$. Susceptibilities for burnt surface soil (0–2 cm) material range from 1 to $33 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$, (I_{RS} from 9 to over $50 \times 10^{-3} \text{ A.m}^2 \text{ kg}^{-1}$). Small pockets of baked, exposed and highly magnetized orange subsoil give rise to local anomalies of over 1000 nT in the strength of the earth's magnetic field and can be readily detected *in situ* using a portable Proton Magnetometer. Magnetic enhancement of soil by the fire is illustrated in Fig. 2 which plots the down-profile variation in specific susceptibility from a locality

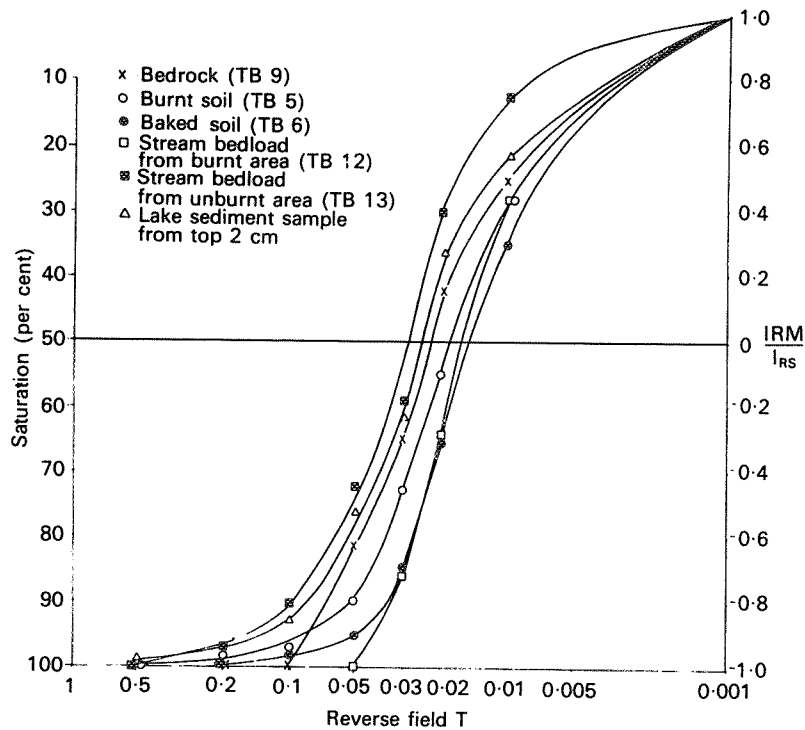


FIG. 3. Llyn Bychan catchment. Coercivity of IRM (B_{CR}) profiles for a variety of materials.

where burnt soil had been subsequently covered over as a result of rapid erosion on the steep slopes above which have been stripped bare of vegetation by the fire. Stream bedload derived from the burnt areas has enhanced susceptibility values, and a twenty-fold increase in I_{RS} in the top 2 cm of a sediment core taken from the centre of the lake in November following the August fire points to the almost immediate transfer of some burnt material to the lake bed.

Fig. 3 plots coercivity of I_{RS} profiles for a selection of samples from the Llyn Bychan catchment and lake. All show a rapid change in isothermal magnetic remanence in low fields and all become 90% to 100% saturated in a field of 0.1T. Coercivities between 0.01 and 0.04T coupled with the high percentage saturation in a field of 0.1T indicate that all the material measured, even the bedrock, is relatively poor in antiferromagnetic minerals (*cf.* Table 3). Burnt soil and stream bedload samples derived from the fire show the lowest coercivities (0.01 to 0.2T) and are fully saturated in fields at or below 0.1T. These features, together with the greatly increased χ and I_{RS} values associated with the fire, point to the formation of secondary ferrimagnetic oxides from soils and parent material, iron rich, but initially poor in both ferrimagnetic and antiferromagnetic minerals. Mössbauer samples TB3 and TB7 are from the top 5 cm of burnt soil, TB1 from the bedload of a stream draining an area of exclusively unburnt soil.

Annecy

Several hundred soil, stream and bedrock samples have now been studied from the region as part of a larger project designed to use magnetic minerals both in the sediments of the Lac d'Annecy and in its drainage basin as an aid to estimating variations in the rates and types of erosion resulting from land use changes in recent times. Bedrock samples from the region are almost entirely diamagnetic Jurassic limestones and either weakly or non-magnetic shales, with susceptibility values

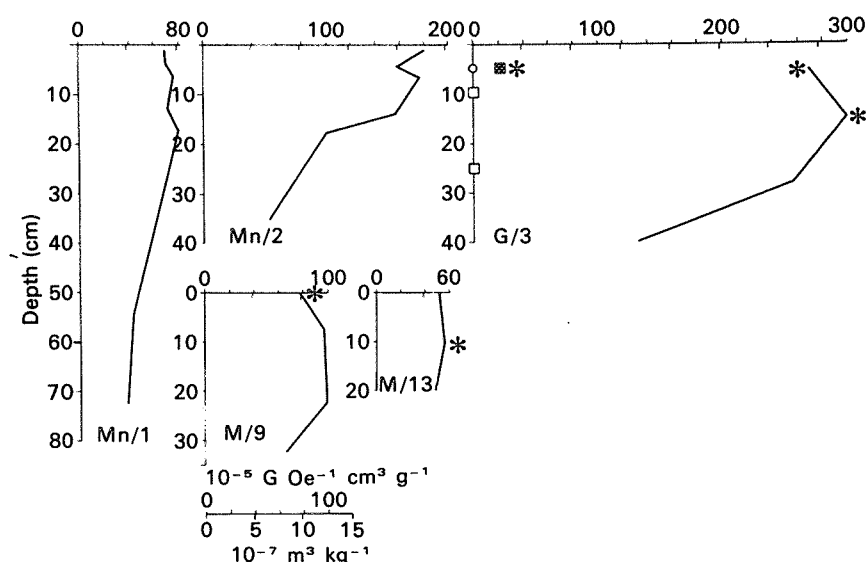


FIG. 4. Annecy region. Magnetic susceptibility profiles from a representative series of bulk soil and extracted rock samples; the samples used for further study are identified with an asterisk. For washed rock fragments from G/3, \circ is calcareous, \blacksquare non-calcareous and \square both types.

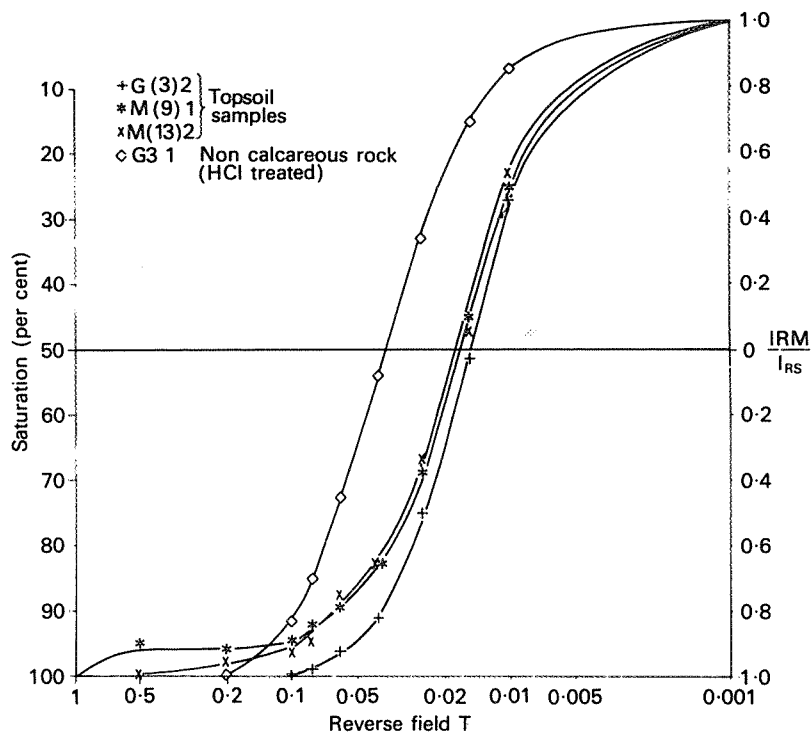


FIG. 5. Annecy region. Selected coercivity of IRM (B_{cR}) profiles for topsoil and rock samples.

ranging from ~ 6 to $12 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$. Soil samples often have susceptibility values at least an order of magnitude higher than the associated bedrock. Fig. 4 shows susceptibility values for soil and bedrock samples illustrative of these generalizations and includes measurements from the two profiles G/3 and M/13 which yielded the magnetic extracts for thermomagnetic study. Fig. 5 plots B_{cR} for three soil samples, one from each of the soil profiles plotted in Fig. 4, as well as for the most strongly magnetic bedrock fragment measured. The three soil samples show uniformly low coercivities (0.02T) though two remain unsaturated at 0.1T indicating a significant haematite content. The rock sample has a much higher coercivity and remains only 70% saturated in a reversed field of 0.1T. The susceptibility and IRM data point to the transformation in the soil of weakly or non-magnetic iron compounds to strongly ferrimagnetic forms. For the magnetic enhancement of the Annecy soils, it is not yet possible to estimate the relative importance of former burning as part of land management, as against more gradual pedogenic processes.

Thermomagnetic experiments

Magnetite, maghemite and haematite exhibit different variations of magnetization with temperature. Pure magnetite has a Curie point of 850K, the Curie point of haematite is 950K, whilst pure maghemite inverts to haematite around 550–700K.

The soil extracts were subjected to a heating and cooling cycle in air in a steady magnetic field of 1.4T, while their magnetization was monitored on a horizontal

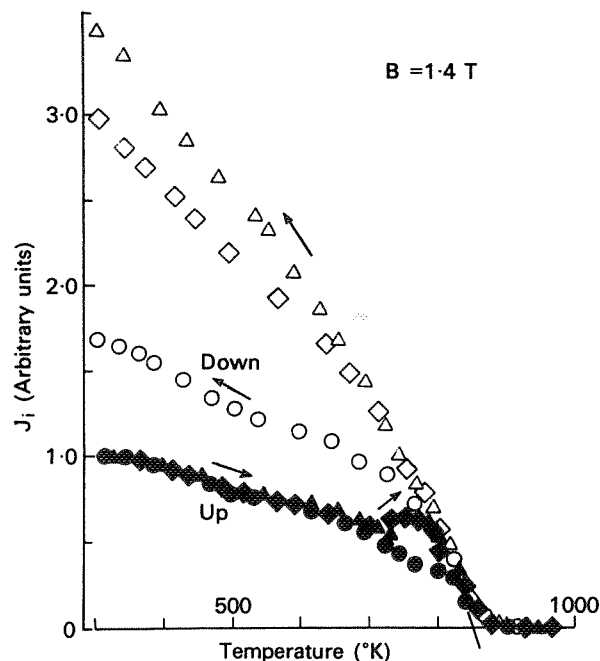


FIG. 6. High field susceptibility (J_i) against temperature changes measured on translation Curie balance. Closed symbols – heating; open symbols – cooling. Circles – Caldy Hill extract; triangles – Annecy M/13/2; diamonds – Annecy – G/3/1. Original, room temperature high field susceptibility normalized to starting value of 1.0.

translation Curie balance. Each heating cycle was made at a rate of about 20°-per minute. The results are shown in Fig. 6.

The Caldy Hill magnetic extract shows a clear Curie point near 850K. On cooling, the thermomagnetic curve is seen to be non-reversible. At room temperature the increase in magnetization is 70 per cent above the original value. This increase has resulted from paramagnetic material or antiferromagnetic haematite being converted at high temperature to ferrimagnetic magnetite. The non-magnetic residue shows an increase of around 2500 per cent above the initial room temperature magnetization following the cycling to 1000K.

Thermomagnetic curves for Annecy samples G3/1 and M 13/2 are similar to those from Caldy Hill. However, there is an increase in magnetization with increasing temperatures in both samples near 720 K. This increase is due to growth of magnetite and complicates an estimation of the Curie point of the natural extract. But again a value close to 850 K is most probable. The increases, after thermal cycling, above the initial room temperature magnetizations, are 200 per cent and 250 per cent for the magnetic extracts for G3/1 and M13/2 respectively.

The thermomagnetic properties of all three extracts can be satisfactorily explained by magnetite being the dominant magnetic carrier. The high Curie point suggests that the magnetite is reasonably free from impurities. The thermomagnetic experiments shows that maghemite is most unlikely to be an important magnetic mineral in these samples because both in natural (*e.g.* Lowrie, 1974) and artificial samples it typically inverts on heating in air to iron minerals of lower magnetization. Mag-

hemite doped with sodium or magnesium is stable up to very much higher temperatures (Stacey and Banerjee, 1974).

Mössbauer effect studies

Although it is difficult to distinguish maghemite from magnetite when present in impure finely divided form in soils, Longworth and Tite (1977), with the use of Mössbauer spectroscopy, have shown that a soil sample after undergoing a laboratory heating procedure (825 K in an atmosphere of nitrogen followed by air) designed to simulate approximately the conditions thought to occur in the field (Tite and Mullins, 1971) contained a large fraction of maghemite. In addition a sample of topsoil taken from an archaeological site was also shown to contain maghemite with the implication that this has been produced by the action of fires during the site occupation. In the present work we have made similar measurements on soil samples taken from regions of recent forest or heathland fires and from the Annecy region.

Mössbauer spectroscopy relies on the use of highly monochromatic gamma rays to measure the tiny perturbations of the nuclear energy levels by the surrounding electrons, the hyperfine interactions, which give rise to an absorption spectrum which is characteristic of a given compound (see *e.g.* Greenwood and Gibb, 1971). The effect is specific to certain gamma rays from certain radioactive isotopes of which the most useful is ^{57}Fe with the gamma ray at 14.4 keV. The absorption spectrum is measured by modulating the gamma ray energy via the Doppler effect by mounting the ^{57}Fe source on an electromagnetic vibrator. The soil samples may be used directly as absorbers, there being sufficient ^{57}Fe in the soil to give a measurable spectrum. In such soils the iron occurs both as free iron oxides and as substitutional impurities in the clay minerals, so-called structural iron.

The hyperfine interactions may be divided into three types, the isomer shift, electric quadrupole interaction and the magnetic hyperfine interaction. Of these the isomer shift displaces the centroid of the Mössbauer spectrum, while with ^{57}Fe the latter two interactions split the Mössbauer line into either a doublet or a six line pattern respectively. The quadrupole doublet occurs for example when the iron atoms sit on sites of non-cubic symmetry, such as those of structural iron, while the magnetic iron oxides each give rise to a six line pattern, whose splitting is determined by the magnetic hyperfine field. When the oxides are finely divided ($<300 \text{ \AA}$) they may behave as superparamagnets in a Mössbauer measurement (see *e.g.* Kündig *et al.* 1966). When the hyperfine field direction changes at a rate of $>10^8 \text{ s}^{-1}$, the magnetic splitting is destroyed and the spectrum reverts to a single line or quadrupole doublet. The Mössbauer spectrum is also sensitive to the presence of impurity atoms via their effect (*e.g.* on the hyperfine field) so that it is frequently difficult to distinguish the different iron oxides in soils on the basis of their Mössbauer spectra. In the work of Longworth and Tite (1977) it was shown that the application of a large magnetic field to the soil samples could be used to distinguish ferrimagnetic and antiferromagnetic oxides.

Experimental method

The soil samples were sieved through a $125 \mu\text{m}$ sieve and dispersed in vacuum grease to make absorbers approximately 100 mg cm^{-2} . In this way absorbers were prepared from the original material and from the material after magnetic separation. The Mössbauer spectra were measured using a source of about $50 \text{ mCi } ^{57}\text{Fe}$

TABLE 2

Hyperfine parameters derived from fits to room temperature spectra of soil samples. H is the hyperfine field, S is the isomer shift, Q the quadrupole interaction given by the difference in separation between lines 1 and 2 and 5 and 6 in a combined magnetic and quadrupole spectrum. Δ is the splitting of the quadrupole doublet

Sample	Magnetic components				Non-magnetic components		
	H (T)	S (mm s ⁻¹)	Q (mm s ⁻¹)	Relative area	Δ (mm s ⁻¹)	S (mm s ⁻¹)	Relative area
TB1	—	—	—	—	0.80	0.18	63%
					2.60	1.07	37%
TB3	51.7	0.27	0.36	12%	0.88	0.26	59%
	49.3	0.23	0.16	16%	2.40	1.00	6%
	45.7	0.49	0.04	7%			
TB7	51.5	0.27	0.24	7%	0.82	0.26	51%
	49.4	0.26	0.12	23%	2.72	0.95	7%
	46.0	0.25	0.04	16%			
Caldy Hill	51.4	0.26	0.32	44%			
	48.9	0.19	0.12	28%	0.76	0.23	12%
	45.8	0.56	0.04	16%			
Annecy	49.2	0.27	0.31	24%	0.61	0.24	18%
					2.65	1.00	12%

diffused into rhodium foil and a conventional constant acceleration Mössbauer spectrometer (obtainable from Harwell Scientific Services). Spectra were recorded at room temperature, at 4.2 K using a liquid helium cryostat and at 4.2 K with a field of 3T applied to the absorber in a direction parallel to that of the gamma ray beam (Figs. 7–11). The spectra were fitted to Lorentzian lineshapes using a least squares minimisation routine. The derived hyperfine parameters are tabulated in table 2 and the fits are shown as solid lines in the figures. Also included for comparison with the 4.2 K spectra are similar spectra for pure bulk oxides.

Results and discussion

Comparison of Figs. 7 and 8 illustrates the effectiveness of the magnetic separation technique for samples from Annecy, Llyn Bychan (TB3 and TB7 both samples of burnt surface soil) and Caldby Hill (1976 burn), through the observed increase in the percentage Mössbauer absorption. This increase is less for TB1, a stream bedload sample from an unburnt part of the Llyn Bychan catchment. Here the material is either paramagnetic or superparamagnetic at room temperature. The increased Mössbauer absorption is due mainly to the removal of some of the non-iron compounds which, while not producing any Mössbauer absorption, will increase the background (photoelectric) absorption.

We consider first those room temperature spectra which contain six line magnetic patterns, Annecy, TB3, TB7 and Caldby Hill, the last three of which are directly associated with recent burning. Apart from these magnetic components (1) there are three other components. Component (2) is a central quadrupole doublet whose amplitude is seen to decrease on cooling the samples to 4.2 K. At the same time the relative amplitude of the magnetic component increases. Such a feature

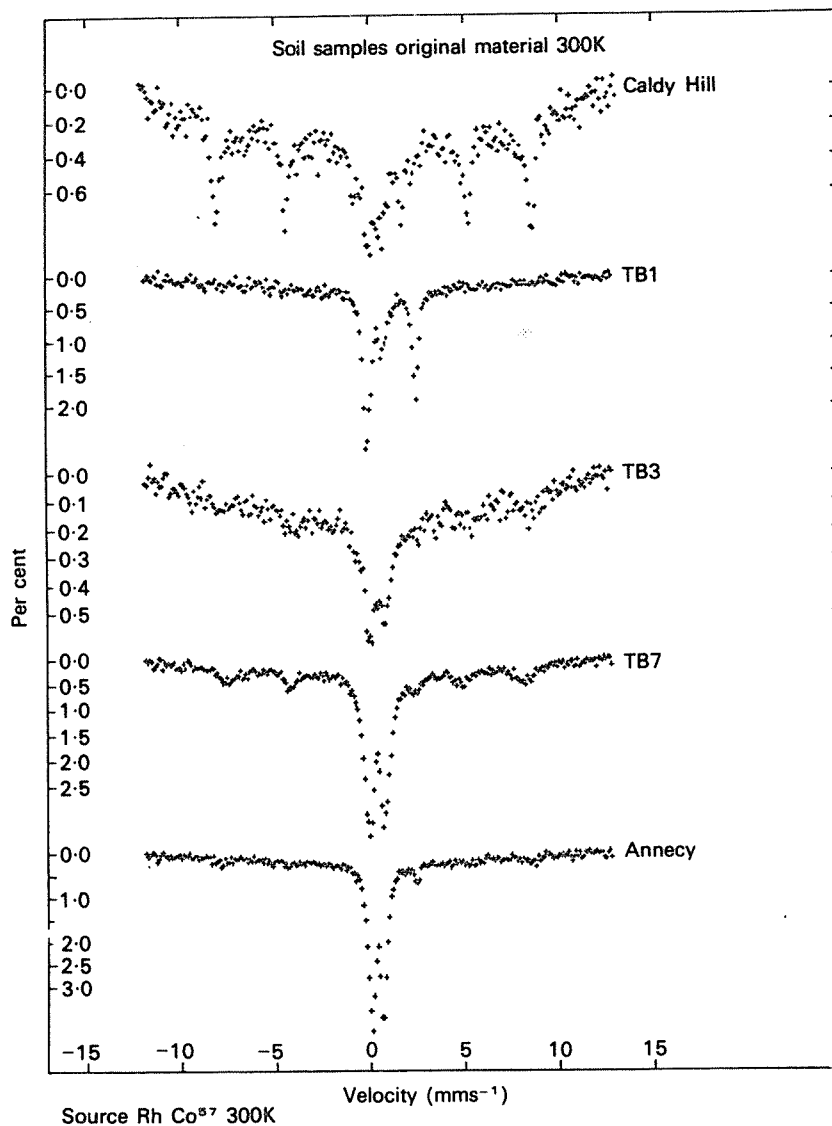


FIG. 7. Iron-57 Mössbauer spectra at room temperature for original samples. The zero of the velocity scale refers to the isomer shift of iron metal. The Caldý Hill sample and the Llyn Bychan samples TB3 and TB7 are from surface soils (0–2 cm) burnt in 1976. Llyn Bychan sample TB1 is stream bedload from an unburnt area.

suggests that at room temperature at least part of the quadrupole double is due to a superparamagnetic iron oxide, while at 4.2 K the rate at which the magnetisation and hence the hyperfine field directions are flipping, has decreased sufficiently for a magnetic pattern to be observed for those iron atoms. The fact that both a superparamagnetic (2) and a magnetic (1) pattern are observed at 300 K

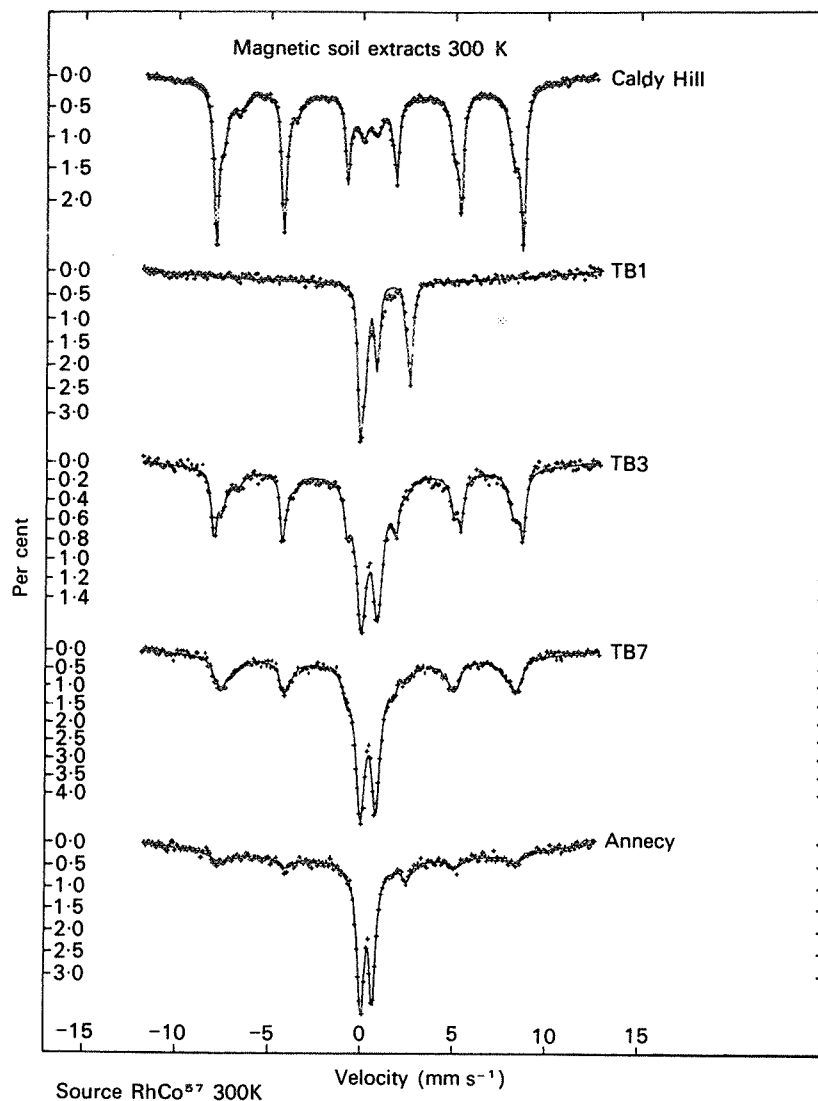


FIG. 8. Iron 57 Mössbauer spectra at room temperature for magnetically separated extracts. The solid line indicates the least squares fit to the data points.

is due to a range in the particle sizes present. It is known that the spin flip frequency depends also on the particle size. Thus we conclude that the average oxide particle size increases in the sequence Annecy, TB7, TB3 and Caldý Hill. The remainder of the 300 K doublet, component 3, and essentially all the 4.2 K doublet, is due to structural ferric material which has a very similar splitting to that of the superparamagnetic doublet (2). In addition there is a weak quadrupole doublet (4) (splitting 2.5 mm s^{-1}), due to structural ferrous ions (see particularly the TB1 spectrum).

The magnetic patterns observed at 300 K may in fact be fitted to three sets of

six line patterns for TB3, TB7 and Caldý Hill (Fig. 9), and one six line pattern for Annecy. Comparison of the observed parameters with those of iron oxides (Kündig *et al.* 1966 and Volenik *et al.* 1975), suggests that one pattern arises from haematite while the remaining two are produced by magnetite. It is known that in magnetite the iron atoms sit on two different types of site giving rise to two differing sets of hyperfine parameters. The relative area under a given Mössbauer pattern, for example a six line pattern, is approximately proportional to the number of iron atoms present in the respective compound on that site. For pure magnetite the area ratio ($H \cong 46\text{T}/H \cong 49\text{T}$) is 2 while the observed ratio is about 0.6 (Table 2). Thus it is possible to say that the magnetite deviates from stoichiometry and may be represented by the approximate formula $\text{Fe}_{2.9}\text{O}_4$. The remaining sites on the spinel lattice will be occupied by vacancies and/or impurity atoms. This completes the identification of the room temperature magnetic components in the Mössbauer spectra.

The spectra at 4.2K (Fig. 10) were fitted to two quadrupole doublets and one six line pattern in order to determine the amount of structural iron. No more sophisticated model was used since the spectrum for pure magnetite at this temperature is extremely complex having at least six six-line patterns (Rubinstein and Forester, 1971). In the present samples the magnetite is impure and the spectrum is further complicated by the presence of overlapping lines due to haematite. Thus it is extremely difficult to use the 4.2 K spectra to distinguish between magnetite/maghemite and haematite in soil samples. We have seen that the magnetic fraction in the 300 K spectra has been identified as being due mainly to magnetite (except for the Annecy sample) (Table 3), and thus we now need some way of determining the nature of the superparamagnetic component. It is possible to do this from the behaviour of the 4.2 K spectra when a large magnetic field is applied to the sample. The relative areas of the six line magnetic patterns are expected to be 3:2:1:1:2:3 where the 3d spins and hyperfine field directions are

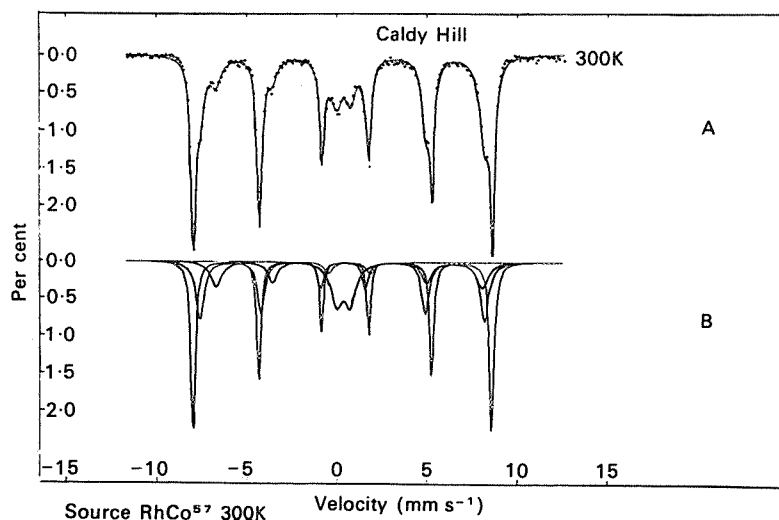


FIG. 9. Iron-57 Mössbauer spectra at room temperature of Caldý Hill samples: A: total fit (as Fig. 8), and B: subsidiary fits for individual compounds.

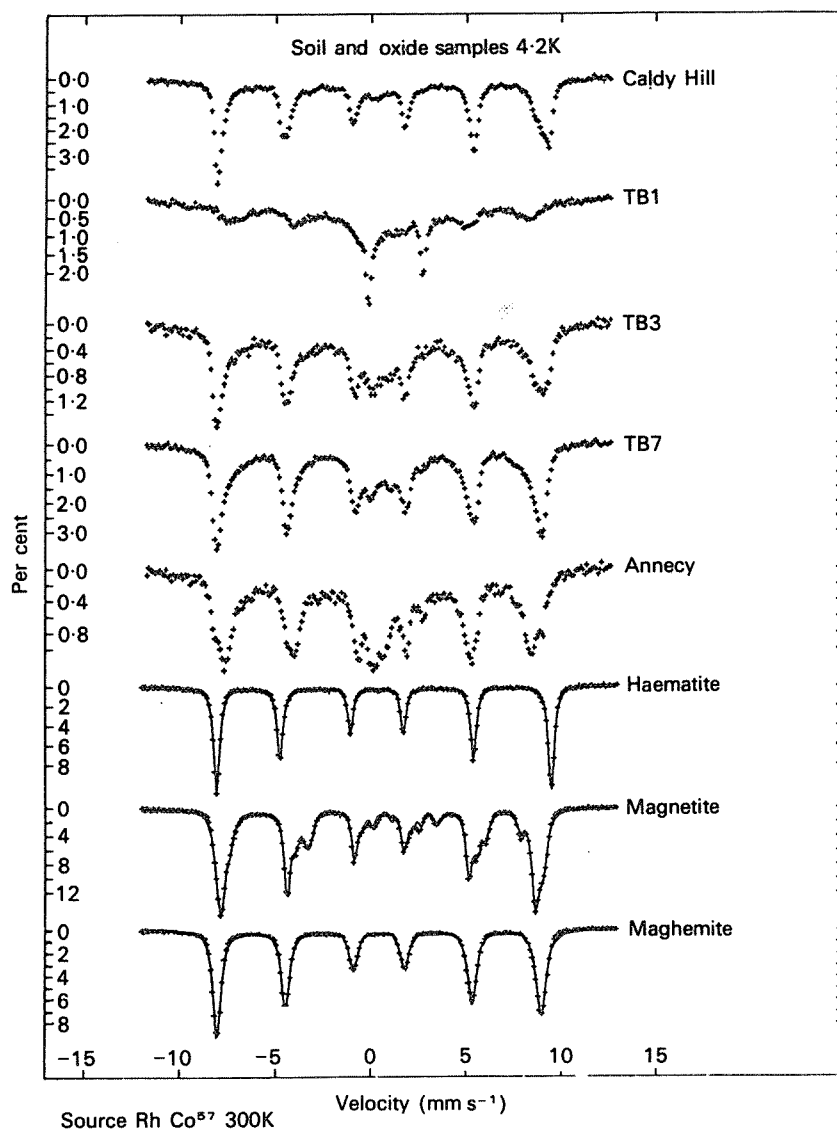


FIG. 10. Iron-57 Mössbauer spectra at 4.2 K for magnetically separated samples and for oxide standards.

completely random e.g. in a unmagnetised ferromagnet or antiferromagnet. If all the field directions are aligned parallel to the gamma ray direction, then these relative areas become 3:0:1:1:0:3. This will occur for ferrimagnets such as magnetite for an applied field $>1\text{T}$ but in general the internal field directions in an antiferromagnet will be unchanged in such an applied field. For this case the spectrum is expected to be unchanged as far as the area ratios are concerned. Thus the two oxides may be distinguished by applying a large external magnetic field. There is one complication however, in that when a ferrimagnetic oxide is finely

TABLE 3
Assignment of relative areas from different phases in the Mössbauer spectra

Sample	Haematite	Magnetite	Superparamagnetic iron	Structural iron	
				Ferric	Ferrous
TB3	18%	34%	29%	15%	4%
TB7	3%	39%	41%	10%	7%
Caldy Hill	44%	44%	7%	5%	—
Annecy	24%	—	46%	18%	12%

divided the alignment of spins may not be complete (Coey, 1971). Longworth and Tite (1977) observed patterns with relative areas of 3:1:1:1:1:3 for such oxides in a field of 3T.

The spectra observed here at 4.2 K in a parallel field of 3T (Fig. 11) were fitted to one set of six lines in order to determine the relative areas of components 2 and 5. For samples TB3, TB7, Caldý Hill and Annecy these were found to be about 1.1, 1.1, 1.5, and 1.2. The predicted intensity for Caldý Hill is approximately $44/88 \times 1$ (magnetite) + $44/88 \times 2 = 1.5$ (haematite) as observed. It is assumed that the superparamagnetic component is magnetite, as is the room temperature magnetic fraction. In the same way if it is assumed that all the superparamagnetic oxide is magnetite then relative areas 1.2, 1.0 and 1.3 are predicted for TB3, TB7 and Annecy. This assumption gives the closest agreement with the observed values of 1.1, 1.1 and 1.2. Thus the relative areas due to magnetite in Table 3 after inclusion of the superparamagnetic fraction will be 63 per cent, 80 per cent and 46 per cent for TB3, TB7 and Annecy respectively.

Finally the room temperature spectrum for TB1 is seen to contain no magnetic component although at 4.2 K about 40 per cent of the total area is made up of a magnetic component. At this temperature the hyperfine field has a value of 48.3T with a quadrupole interaction $Q = 0.36 \text{ mm s}^{-1}$. A smaller amplitude for the magnetic pattern was observed at 77 K which suggests again a superparamagnetic behaviour but with a much smaller particle size than in the other soil samples. It is likely that even at 4.2 K the spin flip rate is not sufficiently slow for the full value of the hyperfine field to be observed. The appearance of the spectrum in an applied field suggests that this component is due to an antiferromagnetic oxide, either haematite or possibly goethite ($H = 50.5 \text{ T}$ at 4.2 K for bulk material).

The soil samples are shown to contain a mixture of iron oxides and structural iron. For samples TB3, TB7, Caldý Hill and Annecy the relative component areas due to magnetite are 63 per cent, 80 per cent, 51 per cent and 46 per cent and due to haematite 18 per cent, 3 per cent, 44 per cent and 24 per cent. The spectra observed for the magnetite component suggests a deviation from stoichiometry, i.e. an approximate formula $\text{Fe}_{2.9}\text{O}_4$. The identification of magnetite is based on the interpretation of the room temperature spectra where its expected contribution is straightforward. There is no evidence for maghemite in these spectra.

Conclusions

Susceptibility, I_{RS} and B_{CR} measurements indicate that in the three areas studied magnetic enhancement has taken place in the soils as a result either of

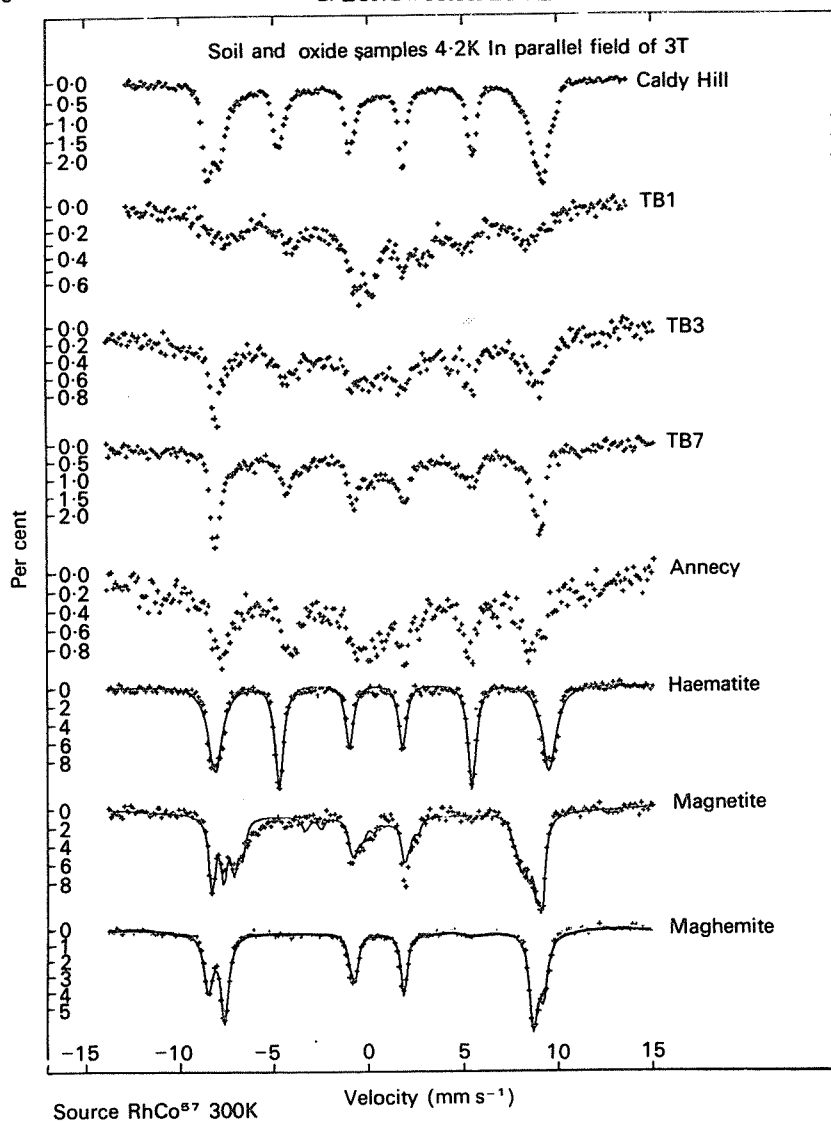


FIG. 11. Iron-57 Mössbauer spectra at 4.2 K with an applied field of 3T in the gamma ray direction, for magnetically separated samples and for oxide standards.

burning or, perhaps in the Annecy soils, more gradual pedogenic processes. In each area, B_{cR} spectra profiles in particular indicate qualitative differences between parent material and enhanced topsoil. These qualitative differences, taken together with the increased susceptibility values, point to the conversion of either non-magnetic or antiferromagnetic forms of iron into strongly ferrimagnetic oxides.

Thermomagnetic studies on magnetically enhanced soils from Caldý Hill and Annecy, and Mössbauer effect studies on soils from Caldý Hill and Llyn Bychan concur in demonstrating that the resultant mineral is magnetite. This conclusion

differs from that reached by the majority of authors who have studied secondary ferrimagnetic oxides in soils and, following Le Borgne (1955, 1960), have inferred the formation of maghemite. Evidence for the relative purity and for the deviation from stoichiometry of the secondary magnetite identified in the present studies remains somewhat conflicting though not irreconcilable; the results of the thermomagnetic experiments are not incompatible with pure stoichiometric Fe_3O_4 whereas the Mössbauer results clearly indicate a degree of non-stoichiometry. Taken together with the previous Mössbauer studies of Longworth and Tite (1977) and unpublished thermomagnetic experiments on soils used in their studies (Thompson, pers. comm.) it seems reasonable to conclude provisionally that secondary ferrimagnetic oxides resulting from the chemical transformation of iron compounds in soils and bedrock, whether by fire or more gradual pedogenic processes, may occupy a range of positions close to the solid solution series between stoichiometric magnetite (Fe_3O_4) and maghemite ($\gamma\text{Fe}_2\text{O}_3$), and may moreover be affected by varying degrees of impurity as a result of isomorphic substitution of iron by commonly occurring soil cations such as sodium and aluminium. Conclusions derived from Mössbauer effect studies with regard to the non-ferrimagnetic components of the Caldry Hill and Llyn Bychan and Annecy samples are compatible with those derived from the magnetic measurements (cf. Figs. 1 and 3 and Table 2).

The combination of rapid, non-destructive measurements such as I_{RS} and B_{CR} with more sophisticated but also more time consuming thermomagnetic and Mössbauer effect studies on selected samples can be seen to provide an effective means of characterizing both ferrimagnetic and non-ferrimagnetic forms of iron in soils.

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