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Potential and Pitfalls in Establishing the Provenance of Earth-Related Samples in Forensic Investigations

ABSTRACT: Earth scientists are often asked to establish or constrain the likely provenance of very small quantities of earth-related material as part of a forensic investigation. We tested the independent and collective interpretations of four experts with differing analytical skills in the prediction of sample provenance for three samples from different environmental settings. The methods used were X-ray diffraction, scanning electron microscopy, the assessment of pollen assemblages, and structural characterization of organic matter at the molecular level. Independent interpretations were less accurate than those where multiple techniques were combined. Collective interpretation was very effective in the assessment of provenance for two of the three sites where the mineralogy and plant communities were distinctive. At the other site, although the mineralogical analysis correctly identified the Triassic mudstone soil parent material, Carboniferous spores from domestic coal were initially interpreted as deriving directly from bedrock. Such an interpretation could be a common pitfall owing to anthropogenic redistribution of material such as coal.

KEYWORDS: forensic science, soil, palynology, mineralogy, particulates, lignin, TMAH, parent material

The occurrence of earth-related particles such as minerals, pollen/spores, and organic matter together with anthropogenic material on evidential items can help to establish their provenance, contributing to both intelligence and evidential stages of forensic investigations. For example, the search for the body of a murder victim in northern England during March 2005 was based on soil material believed to be from the body deposition site (1).

Earth-related particles recovered from suspects' clothing, footwear, vehicles, or dwellings, and from crime victims are commonly used as comparative material with a crime scene (2). This comparative approach has a number of difficulties, but the application of multiple analytical methods on differing components of an earth-related forensic sample, with careful interpretation, can produce significant findings. Even more challenging are instances where earth-related particles are recovered and an expert is asked to identify where the material may have come from. Without recourse to extensive and up-to-date databases on the properties of the natural fractions in earth-related materials, earth scientists often choose to use a variety of methods to investigate and constrain sample provenance. The study presented here demonstrates the potential and pitfalls in one of the most difficult and challenging tasks for analytical earth scientists; predicting the provenance of a sample of earth-related material.

The majority of soils across the UK (United Kingdom) landscape have developed over 10,000 years since the last ice age, with geochemical and mineralogical characteristics closely related to the parent material from which they formed (3). These parent materials include the underlying bedrock or any overlying Quaternary material such as glacial, riverine, or windblown deposits. Individual parent material units vary in area from a few tens to hundreds of square kilometres. The proportions and characteristics of the dominant minerals (quartz, carbonates, clays) often differ sufficiently in the soils developed over these parent material types for them to be distinguished from one another at a regional scale. Hence, soil mineralogy could constrain potential source areas to a handful of regions based on expert interpretation and comparison with mineralogical databases and national maps showing the distributions of soils and parent material types. As the geology of the UK spans all the geological periods of the Earth's history with a diverse suite of parent rocks making up a relatively small landmass, it is likely to be well-suited to the application of this approach.

The provenance of a forensic sample might be further constrained if information is included on organic matter signatures of the lignin in plant fragments and pollen and spore assemblages. These two techniques are complementary as they provide information on vegetation types at and around the site, respectively. It may then be possible to identify more localized sites within the soil and mineralogical regions that warrant further investigation. Such an approach was successfully demonstrated in locating a burial site based on earth-related particles taken from wheel arches and foot-wells of the vehicle used to dispose of two bodies (4). The basic principle is to use our understanding of the natural distribution of minerals in the soil and material derived from local plant communities to determine the characteristics of the forensic sample location.

In some circumstances, the identification of unusual or "exotic" particles in soil using scanning electron microscopy (SEM) may also provide useful information on the provenance of a forensic sample. Such particles are frequently of anthropogenic origin, such as slags and other industrial by-products. Other natural material may become "exotic" either by being moved from its natural source to an *ex situ* location, or by being altered in some way. For example, the quarrying and crushing of igneous rock to make roadstone produces particles with fresh, angular surfaces.

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The full-range of particle types (minerals, pollen and spores, organic matter, and anthropogenic particles) are typically present in varying proportions in forensic samples collected from, for example, a vehicle wheel-arch or muddied shoe. Although a wide variety of methods are available for the analysis of these components, those adopted may not be entirely complementary, and focus predominantly on one component (e.g., soil minerals and their properties) in a set of samples. Due to financial constraints, investigators may often choose to focus on one or two of these components. A recent study used four techniques (color, particle-size, stable isotopes, and bulk chemistry) to investigate and compare results of an investigation of soil transfer to footwear (2). In this paper, we report on a blind case study in which we aimed to test a range of techniques, both independently and collectively, on the differing components of earth-related forensic samples, to assess their efficacy in providing information on their provenance. One advantage of analyzing samples collected as part of a case study, rather than samples drawn from a real forensic investigation, is that in the latter, the precise provenance of each sample is rarely known, while in the former we can be certain of the source location. In this approach, we chose not to restrict the quantity of forensic sample material to the small quantities that are typically available in forensic investigations (<1 g), as we wished not to constrain the performance of any method. However, recent advances in analytical methods have enabled reliable measurements to be undertaken on increasingly smaller quantities of earth-related material.

We collected small quantities of earth from three locations with differing bulk mineralogy, land use and plant communities, and in one case close to a source of anthropogenic particle emission (a steelworks). The sites were identified and samples collected by geologists who were not experts in the fields of interest. Small subsamples were then provided to experts in X-ray diffraction (XRD), SEM, palynology (the study of pollen, spores, and other organic microfossils) and molecular organic matter analysis. The experts were not given any information on the actual provenance of the samples. Each expert was asked to report on the likely provenance of each of the three samples based on their analysis and was not permitted to discuss their findings. A meeting was subsequently held to pool the findings and to assess the synergy of the various methods in constraining sample provenance.

First, we describe the background to the three sites and how the samples were collected. We provide background information on each of the techniques and how the samples were prepared and analyzed. We then present a summary of each expert independent interpretation of the samples, and highlight both the positive and negative aspects of their findings with respect to provenance of the samples. We then discuss the potential synergy between the methods, and their strengths and weaknesses for investigating provenance in landscapes with characteristics similar to those found in the UK.

Study Sites and Sample Collection

Three sites were chosen to represent differing geological and vegetative environments in the central-eastern region of the UK, with differing potential sources of anthropogenic contamination. The characteristics of the geological parent materials, vegetation types, and source of anthropogenic contamination are summarized in Table 1. The precise sampling locations are shown in the maps in Fig. 1.

The samples for the study were all collected on October 22 and 23, 2003. At each site, clean boots were worn and used to walk repeatedly across a small patch of ground. A clean brush was used to transfer around 20 g of the adhered soil or sediment onto clean paper from the boots, placed in a clean plastic bag, labeled, and sealed. At each location digital photographs were taken of the site and the surrounding vegetation. The dominant, local vegetation types were recorded, but kept confidential, for use in assessing the expert interpretations. Precise geographical coordinates were recorded using a handheld GPS. On return to the laboratory, all samples were placed in a humidity and temperature controlled room to ensure that natural conditions were maintained. Subsamples were taken and provided to each of the four experts to analyze.

Background to the Methods, Sample Treatment, and Analytical Procedures

XRD

Since the early 1990s, XRD has proved to be a highly effective tool for the forensic mineralogist (4–10). XRD analysis is versatile and has the ability to detect any crystalline, or partially crystalline substance whether inorganic, organic, or metal. It has been routinely used in the identification of "contact traces" from a wide variety of materials (6). Analyses may be required to identify a single substance (11,12) or to compare two samples to ascertain whether they have a common source (4,5). Importantly, XRD analysis is able to provide reliable data from small ($<10\,\mu$g)

TABLE 1—*Names and brief characteristics of the geological parent material and plant communities at the three sites.*

Site Name, Number, and Description	Detailed Site Description	Period, Name, and (Stage) of Geological Parent Material and Rock Description	Major Plant Communities
1. Bratt Hill, Scunthorpe (population 172,000)	Next to a footpath in an agricultural field, on the outskirts of Scunthorpe, within 1 km of a steelworks	Jurassic (Sinemurian); Frodingham Ironstone Formation; Quartz-rich ironstone	Agricultural field of unharvested cereals. Grass and nettles nearby. Brambles, blackberries, and long grass on the perimeter of the field. Trees along one boundary of the site
2. Domestic garden, West Bridgford, Nottingham (population 267,000)	Domestic garden in a suburb of Nottingham	Triassic (Carnian); Edwalton Formation; Red-brown mudstone	Apple tree, holly, rhododendron, azalea, buddleia, plum tree, vibernum, pear tree, lilac, foxgloves, oxalis, pieris, grassed lawn *c.* 2 m from sample site, compost heap *c.* 5 m. Bird water bath 10 m from sample location
3. Wollaton Park, Nottingham	Dried sediment at the margin of a lake in a large urban park. 30 cm above current water level	Carboniferous (Duckmantian); Pennine Middle Coal Measures Formation; Interbedded gray mudstones, siltstones and sandstones	Rhododendron/laurel. Alder, beech and oak trees, grass, rotting wood, and leaf litter

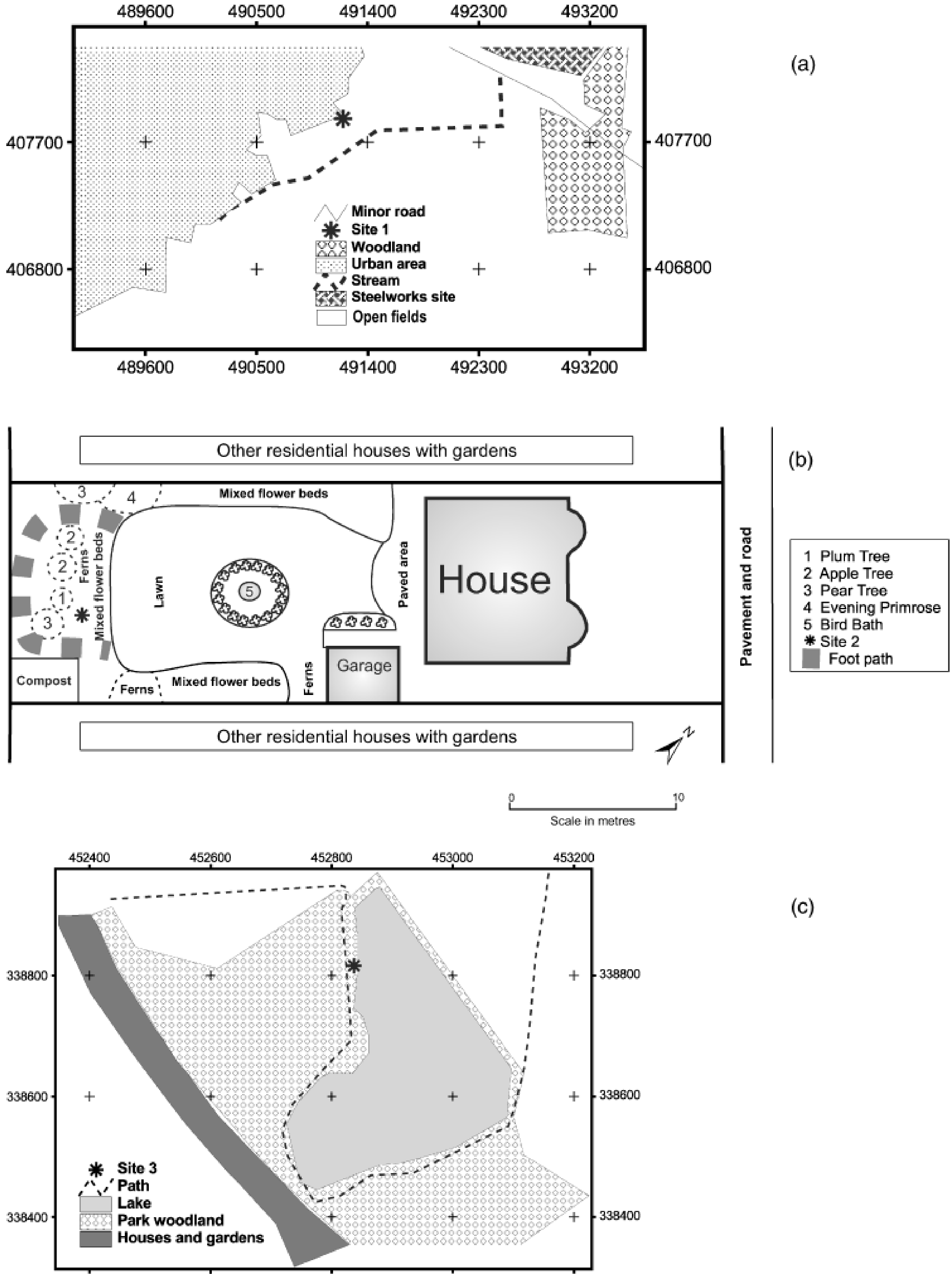

FIG. 1—*Locations of the three study sites in central-eastern England: (a) site 1—a field on the outskirts of Scunthorpe, (b) site 2—a domestic garden in a suburb to the south of Nottingham, and (c) site 3—a large urban park in Nottingham. Grid references are meters of the British National Grid.*

specimens recovered from crime scenes and suspects. The nondestructive nature of the technique is also invaluable where there is a need to apply subsequent analytical techniques.

In the geosciences, XRD remains the best available technique for phase identification in fine-grained materials and is the primary technique for identifying clay minerals, the most abundant minerals at the surface of the Earth (13). Owing to their widespread distribution, small grain size, and variable composition, clay mineralogy deduced from qualitative XRD analysis has often been employed to determine the provenance of rocks and soil samples in forensic cases (4,14,15)

Recent advances in quantitative XRD analysis have extended the applicability of the technique to provide statistical reliability in similar rocks and soils (5). Much of this progress can be attributed to the development of sophisticated Rietveld refinement software packages (e.g., Siroquant offered by Sietronics, TOPAS from Bruker AXS and HighScore Plus from PANalytical). Quantification using Rietveld refinement (16) avoids the need to produce synthetic mixtures and involves the least squares fitting of measured to calculated XRD profiles using a crystal structure databank. Mineral concentration errors for such an approach are typically $\pm 2.5\%$ for concentrations >60 wt%, $\pm 5\%$ for concentrations between 60 and 30 wt%, $\pm 10\%$ for concentrations between 30 and 10 wt%, $\pm 20\%$ for concentrations between 10 and 3 wt%, and $\pm 40\%$ for concentrations <3 wt% (17).

The three subsamples were removed from their sample bags, dried at 55°C overnight, visually described using a binocular microscope, and then crushed in a pestle and mortar to *c.* <2 mm. For the whole-rock analysis, a representative, *c.* 2 g subsample was isolated using a riffle-splitter and powdered using a pestle and mortar to $<125\,\mu$m. To ensure a finer and uniform particle-size for whole-rock XRD analysis, the powders were then wet micronized under acetone in a McCrone micronizing mill for 10 min. The resulting slurries were dried, disaggregated, and then back-loaded into standard aluminum sample holders. XRD analyses were carried out using a Philips PW1700 series automatic diffractometer (Philips, Almelo, The Netherlands) equipped with a cobalt target X-ray tube and operating at 45 kV and 40 mA. Diffraction data were analyzed using PANalytical X'Pert software coupled to the latest version of the International Centre for Diffraction Data (ICDD) database. The whole-rock samples were scanned from 3° to 65° 2θ at a scanning speed of 0.8° 2θ/min. Following identification of the mineral species present in the samples, whole-rock mineral quantification was achieved using the Rietveld refinement technique using Siroquant v.2.5 software.

In order to determine the nature of any clay minerals present in the samples, a further *c.* 5 g subsample was dispersed in deionized water using a combination of reciprocal shaking and ultrasound treatment. The resulting dispersion was then sieved to $<63\,\mu$m and the material placed in a 100-mL measuring cylinder with 0.5 mL 0.1 M sodium hexametaphosphate ("Calgon," $(NaPO_3)_6$) solution to disperse the individual clay particles and prevent flocculation. After standing for a period determined from Stokes' Law, a nominal <2-μm fraction was removed and dried at 55°C. Approximately 15 mg of the dried <2-μm material was then Ca-saturated using 1 M $CaCl_2 \cdot 6H_2O$ solution. To achieve full saturation, the solution was replaced three times with fresh $CaCl_2$ and the material then washed with deionized water to remove all traces of reagent. The material was then resuspended in a minimum of distilled water and pipetted onto a zero-background silicon crystal substrate to produce an oriented mount. The mounts were allowed to dry at room temperature before analysis.

The oriented Ca-mounts were scanned from 2° to 32° 2θ also at 0.6° 2θ/min after air-drying, ethylene glycol-solvation, and heating to 550°C for 2 h. Ethylene glycol-solvation was achieved by placing the samples in a desiccator filled with the reagent and heating to 55°C overnight. Clay mineral identification was achieved by careful measurement of characteristic basal *d* spacings and their reaction to the diagnostic testing program.

SEM

The principle of SEM is to scan an accelerated beam of electrons over the surface of a specimen. The electron beam interacts with the specimen to produce various types of electron emissions, which can then be used to produce images at much higher spatial resolution than can be achieved using conventional optical microscopes. The interaction also produces X-rays with energies characteristic of the elements present in the specimen. This allows chemical analysis to be performed on selected areas of the specimen.

SEM has many applications in soil analysis. It can be used to image surface topography in order to characterize grain surface textures, surface coatings, and diagenetic features (18). It can also be used to produce images in which brightness is a function of atomic density, revealing the spatial relationships between different minerals and phases to be imaged. This is especially useful for finding rare, high atomic density materials such as heavy metal-bearing particles (19). Recently, automated analysis of characteristics such as grain size, shape, chemistry, or phase composition has become more practicable. This is beginning to have an impact in forensic geoscience because it has the potential to reduce analytical time and operator subjectivity and improve repeatability (20,21).

SEM techniques have been extensively used in forensic science (22,23) and in some cases have become standard, for example in the analysis of gunshot residue (24). SEM has been applied to forensic soil analysis in numerous legal cases and a small amount of research and case material has been published (20,21,25–27). While numerous publications have demonstrated the utility of SEM in forensic soil analysis, researchers have not published the results of any blind testing under realistic conditions (21,26).

Firstly, a visual inspection of the samples was carried out with the aid of a ×10 magnification hand lens. Any unusual particles were described and a selection taken for further SEM examination. Basic observations were made of the mineral fraction of the samples, but organic materials were not examined in great detail.

Large organic particles were removed and a sub-sample of the remaining sand and silt-grade material was sprinkled over an aluminum stub mount on which a sticky carbon film had been placed. The selected unusual particles were similarly placed on a second stub mount. The stub mounts were then briefly examined under a binocular microscope. SEM analysis was performed using a Leo 435VP SEM operated at 20 keV under "variable pressure" conditions. Conventional SEM requires the sample chamber to be kept under high vacuum conditions such that nonconducting samples must be coated with a thin conducting film such as gold or carbon to draw off excess charge as the electron beam hits the material. The "Variable Pressure" SEM is capable of operating under conditions much closer to atmospheric pressure (in this case about 0.3 Torr) with only marginal loss of spatial resolution. The significant outcome for forensic analysis is that samples do not need to be coated and so the analysis is nondestructive and samples can be recovered later. Imaging was performed using both a secondary electron detector, which produces images emphasizing topography, and a back-scattered electron detector, which produces images whose brightness is a function of the atomic density of the material. Qualitative chemical analysis of individual grains was carried out using an Oxford Instruments ISIS 300 energy-dispersive X-ray spectrometer. It is not possible to obtain reliable quantitative chemical compositions of materials by electron beam methods unless they have been prepared to present flat, polished surfaces, which would constitute a significant degree of destruction of the sample.

Molecular Organic Matter Signatures

Although the organic matter content of most soils is less than 5% w/w, the information contained within this fraction can help to identify specific plant communities, complementing information from any pollen that may be present. Organic matter in the surface layer of soil is mainly composed of plant biopolymers and their transformation products (28). Lignin, the aromatic biopolymer found exclusively in vascular plants, is routinely used by environmental geochemists as an indicator of vegetation source due to its moderate reactivity, wide spatial and temporal distribution, as well as its characteristic fingerprint of phenolic constituents (29–31). Recently, off-line thermochemolysis with tetramethylammonium hydroxide (TMAH) combined with gas-chromatography/mass-spectrometry (GC/MS) has been applied to the structural elucidation of fresh and altered lignin at the molecular level (30,32). Thermochemolysis with TMAH effectively depolymerizes the lignin macromolecule into small fragments by cleaving propyl-aryl ether bonds and methylates hydroxyl groups located on aromatic rings and alkyl side chains (33).

The procedure is ideally suited to forensic analysis of soil organic matter as it requires only 0.5–5 mg of sample yet provides specific information at the molecular level on lignin (34–36). Three broad vegetation groups are readily distinguished based on the proportions of their methylated phenolic units; (1) gymnosperm woods yield dimethoxyphenol units (G); (2) angiosperm woods produce both G and trimethoxyphenol units (S); and (3) monocotyledons such as grasses produce S, G, and monomethoxyphenolic units (P) (37) and references therein. Additional information from cinnamic acids (C), which link lignin to polysaccharides in vascular plants, can also be used in combination with the three lignin phenolic units to further characterize plant materials in soils. Studies using thermochemolysis have also demonstrated that the product profile generated from heartwood of five softwoods, three European hardwoods, and four Australian *Eucalyptus* can be used to differentiate woods at the genera and, in some cases, species level (34). Increases in the relative intensity of phenolic acids to aldehydes are indicative of oxidative fungal decay which provide a further chemical descriptor for comparative purposes (38,39).

Powdered samples (3–5 mg in weight) were placed in individual reaction vessels with 100 µL of TMAH solution (25% w/w in methanol). The TMAH preparations were left overnight in a vacuum desiccator in the presence of P_2O_5 in order to facilitate thorough mixing before the removal of methanol under vacuum. Dried mixtures were sealed under vacuum and heated in an oven at a temperature of 245°C for 30 min. After cooling the vessels were opened and the inner surfaces of the tube washed with 10 mL of dichloromethane. The extract was dried under a stream of N_2 and dissolved in 100 µL of dichloromethane. Volatile products were separated by capillary GC using a fused silica VF-5 ms column (60 m length × 0.32 mm i.d. × 0.25 µm film thickness). The GC oven was operated using the following program: isothermal for 5 min at 40°C; then raised from 40 to 300°C at 4°C/min and held isothermally at 300°C for 10 min with helium as the carrier gas. The GC was directly coupled to a Fisons MD800 mass spectrometer operated at 70 eV with a mass range of m/z 30–550, (trap current 140 µA, source temperature 270°C). Data acquisition and analysis were performed using a Mass Lab data system.

Palynology

Palynology is the study of organic microfossils such as plant spores and pollen and their modern counterparts. It also includes marine and other aquatic organisms, and these organic-walled bodies are collectively known as palynomorphs (40,41). The pollen and spores of different plants are generally morphologically distinctive and can normally be identified to the familal, generic, or specific level. Where the botanical affinities of spores and pollen are known, the palynomorph spectrum can help to reconstruct environments of deposition. The overwhelming majority of Quaternary plant taxa are extant, hence this technique is especially effective in subfossil and modern sediments. There is an extensive literature on the environmental interpretation of Quaternary pollen (42–44). Palynomorphs are numerous, small, robust, and relatively ubiquitous and hence are normally present in sediments, soils, and other materials.

Forensic palynology has been used in numerous criminal cases, largely in New Zealand, the UK, and the US (4,45–49). A comprehensive account of the problems inherent in forensic palynology has been published by Mildenhall (48).

The palynology of each of the three samples in this study was investigated in order to characterize the flora at the sites, in addition to any reworked grains that may indicate the age of the bedrock. The samples were all prepared using the method of Riding and Kyffin-Hughes (50). This technique deflocculates clay using $(NaPO_3)_6$ allowing this fraction to be sieved away, leaving an organic-rich residue. It avoids the use of hazardous mineral acids such as hydrofluoric acid (HF). Permanent microscope mounts of the palynomorph-rich residue were studied using a Nikon Eclipse E600 light microscope (Tokyo, Japan). In order to supplement the palynological data and interpretations, the coarse organic fraction (>500 µm) was studied for each of the three samples. A representative selection of palynomorphs and a diatom are illustrated in Fig. 2.

Results and Interpretation

Before their examination of the samples, the four experts were informed only that each sample had been collected from a unique site on the mainland of England. A comprehensive set of results and interpretation by each expert on the likely provenance of each sample constituents is provided at www.bgs.ac.uk/forensicgeology. These are summarized in Tables 2–4 for Sites 1–3, respectively. For each site, we first highlight those aspects of each of the independent expert interpretations that assisted in constraining provenance, and then any features that would detract from identifying the location of the sites. We then provide the experts' collective interpretation.

Site 1—Bratt Hill, Scunthorpe: Ironstone (See Table 2)

The interpretations of both mineralogical experts (XRD and SEM) positively identified that this soil had developed over a ferruginous sandstone or ironstone of Carboniferous or Jurassic age. The collective interpretation refined provenance to soils overlying Jurassic ironstones, a series of long, but relatively narrow (typically less than 1 km) outcrops of ironstone parent material in eastern and southern England. The other two experts both positively identified the dominant vegetation as grasses, and specifically those related to agricultural crops of wheat, barley, or rye. The actual dominant vegetation at the site was a variety of grasses and cereals. It is noteworthy that in the interpretation of the organic matter it was stated that the plant matter had not undergone extensive microbial alteration; the positive implication is that this may relate to the standing crop grown during the previous months that was present at the site. The pollen analysis

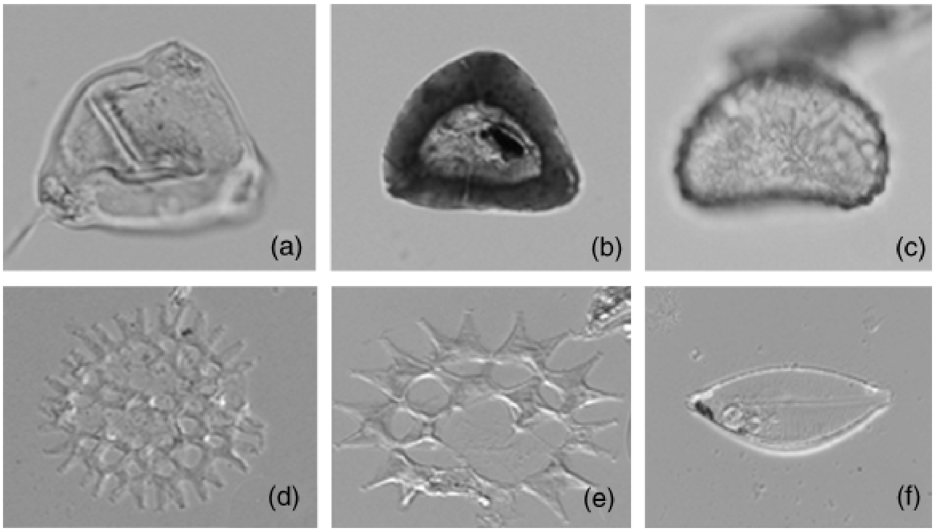

FIG. 2—*A selection of microfossils from sites 2 and 3. These comprise a pollen grain (a) spores (b, c) the freshwater green alga Pediastrum (d, e), and a diatom (f). The photomicrographs a, b, and c were taken using plain transmitted light; d, e, and f were taken using differential interference contrast. All specimens are curated in the palynological collection of the British Geological Survey, Nottingham, UK. (a)* Circaea sp. *This pollen is from a representative of the Evening Primrose family. Site 2. Maximum dimension: 45 μm. Specimen BGS MPK 13,395. (b)* Densosporites sp. *A Carboniferous spore that has been introduced (reworked) into the soil, probably from fragments of domestic coal. Site 2. Maximum dimension: 40 μm. Specimen BGS MPK 13,396. (c)* Polypodium vulgare*. This spore is from the Common Polypody fern. Site 3. Maximum dimension: 60 μm. Specimen BGS MPK 13,397. (d, e)* Pediastrum spp. *Two examples of coenobia of Pediastrum, a genus of colonial green chlorococcalean alga, typical of freshwater habitats. Site 3. d, maximum dimension: 56 μm. Specimen BGS MPK 13,398. e, maximum dimension: 82 μm. Specimen BGS MPK 13,399. (f) Diatom. A silicious frustule of a pennate diatom; these types dominate freshwater/terrestrial habitats. Site 3. Maximum dimension: 93 μm. Specimen BGS MPK 13,400.*

positively identified mixed sources of vegetation (Table 1) that were identified around the site during sample collection.

In the coarse fraction organic material analysis, there are references to brick and slag fragments; the latter may be waste material derived from the Corus UK steelworks. Although the site was within 1 km of the steelworks, no observations were made by SEM of the characteristic fine particulates that are emitted from steelworks furnaces. We might have expected to observe anthropogenic particulates in the soil given that total atmospheric emissions of $<10\,\mu m$ particulates from the Corus UK steelworks in Scunthorpe was 5500 tons between 1998 and 2002 (51). However, this steelwork emission signature becomes very diluted

TABLE 2—*Summary of the four independent expert analyses: Site 1–Bratt Hill, Scunthorpe.*

Method	Results	Expert Interpretation
XRD+optical microscopy	Predominantly composed of ferruginous, well-sorted quartz grains (*c*. 91%) with minor feldspar and traces of other minerals (Fig. 3*a*). Contains little silt- and clay-grade material and sparse organic material. Clay mineral assemblage of major illite and kaolinite and minor illite/smectite and chlorite (Fig. 3*b*)	Appearance and bulk mineralogy suggest that it is derived from a quartz-rich sandstone parent. The clay mineral assemblage suggests that the parent material was unlikely to be younger than Cretaceous, or Lower Palaeozoic or Permo-Triassic. Likely provenance; an organic-poor soil possibly developed from a Carboniferous or Jurassic ferruginous-sandstone
SEM	Minor organic component: stems, skeletal fragments. Mineral component: mostly Fe oxide stained quartz sand with minor silt. Some calcareous ooliths and rare calcareous detrital and bioclastic grains. Coal or soot particles. Fibers. Piece of micaceous siltstone. (Figs. 4*a–c*)	Combination of red sand and calcareous ooliths suggests a Jurassic ironstone parent. These rocks outcrop in a narrow band from East Yorkshire through the East Midlands and the Cotswolds to Dorset
Palynology	The fine-grained organic particles are dominated by plant tissues. Palynomorphs are sparse and are dominated by tree pollen, largely pine. Pteridophyte spores and herbaceous pollen are also present rarely. The coarse organic particles are dominated by degraded cereal/grass straw and chaff, seeds, humus, and sand. Synthetic particles are also present, including white fibers and fragments of brick and slag	The pine pollen may be far-travelled. The remainder of the palynomorph assemblage indicates the presence of ferns, hazel bushes, and herbs such as chickweed. The site sampled clearly lies on, or adjacent to, land where tall grasses dominate the vegetation, because debris from these grasses dominates the coarse fraction. The abundant degraded grass debris with the sand, fibres, brick, and slag is therefore consistent with a densely grassed area with a well-drained soil, close to mixed vegetation and heavy industrial plant
Organic matter	Fig. 5*a* S/G 0.64 C/G 0.25 $(Ad/Al)_G$ 1.3 $(Ad/Al)_S$ 1.2 Γ 0.7	Lignin signature is from nonwoody angiosperm. The closest comparable plant type being from the main stems of grass-related agricultural crops such as wheat and/or barley. The plant matter has not undergone extensive microbial alteration

XRD, X-ray diffraction; SEM, scanning electron microscopy.

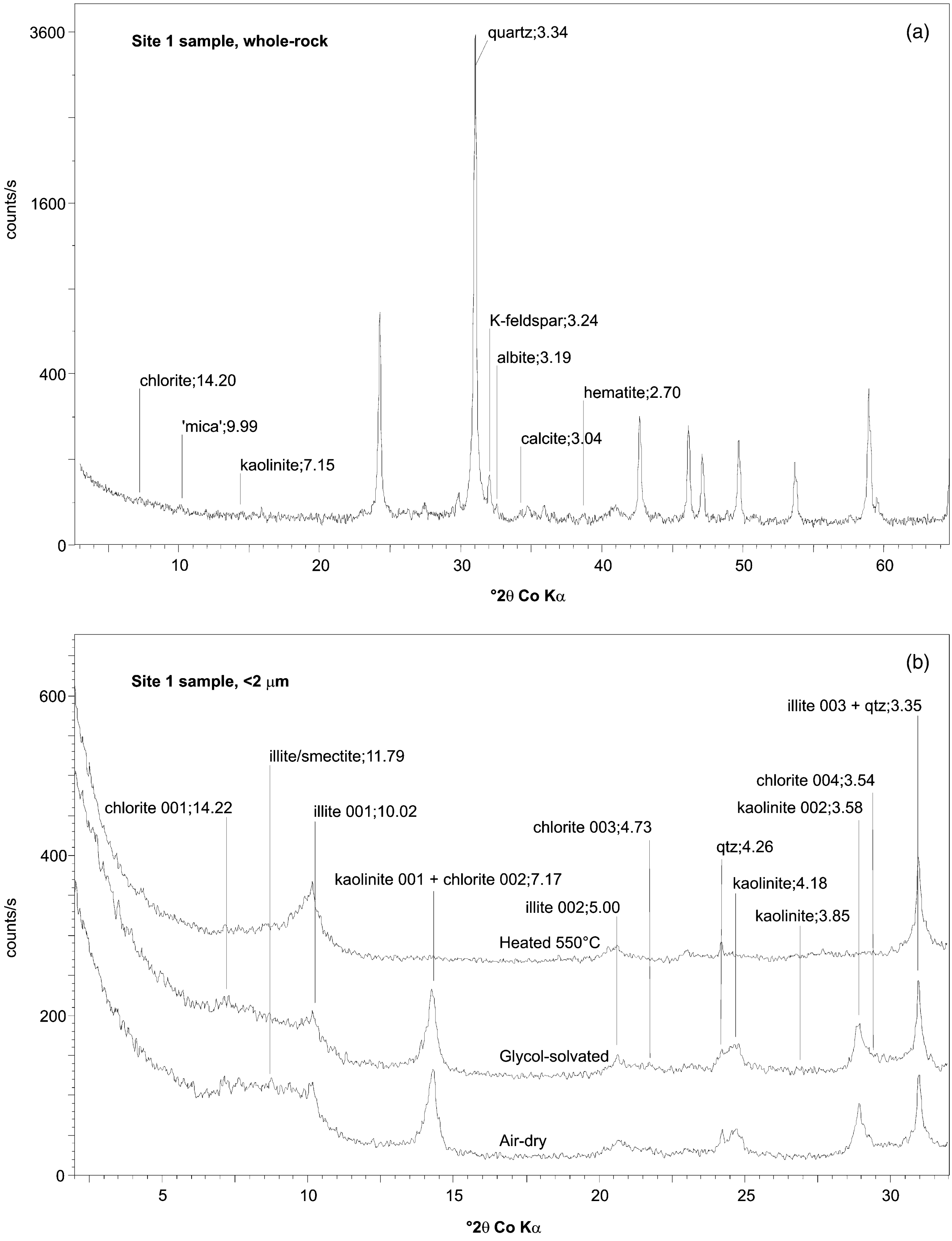

FIG. 3—*X-ray diffraction traces for site 1 sample (a) whole-rock trace, mineral phases are labeled with their most intense/diagnostic peak and corresponding d (Å) spacing (b) air-dry, glycol-solvated and heated 550°C <2 μm traces, diagnostic clay mineral 00l basal spacings are specified with their d (Å) spacing.*

once the material falls out of suspension onto the soil and would normally be found by operating an SEM at particular conditions and systemically scanning for heavy particles, which was not done in this case. In summary, the independent expert interpretations significantly constrained the provenance of the sample to soils over the Jurassic ironstones, a distinctive parent material type, and

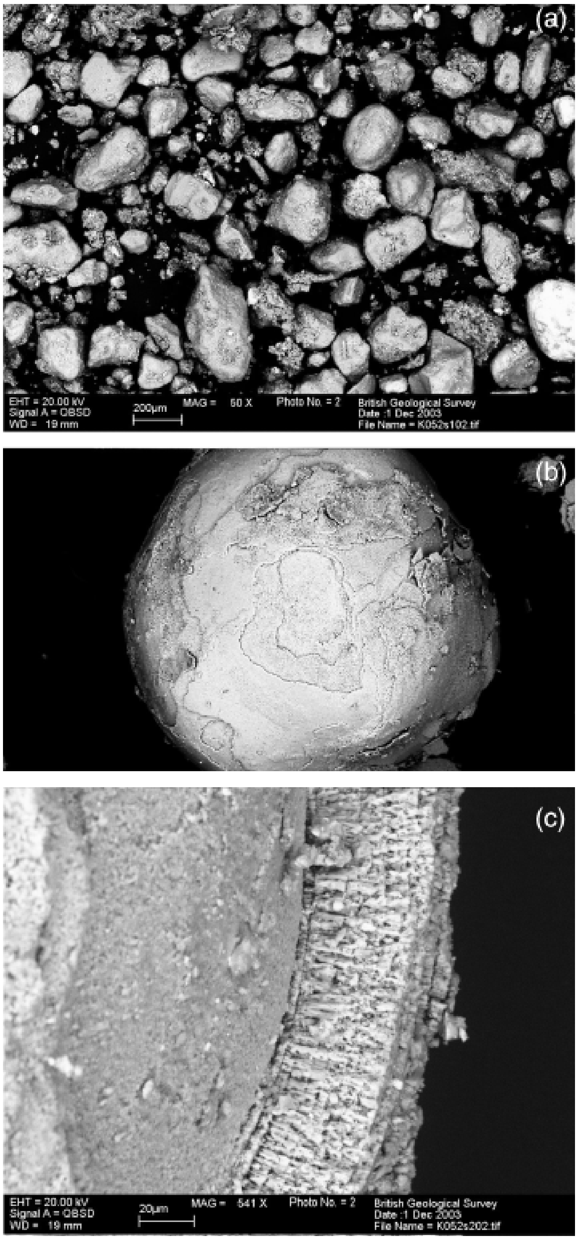

FIG. 4—*Scanning electron microscopy images from site 1 sample: (a) mineral component of the sample, dominated by well-rounded quartz sand (field of view 2.4 mm) (b) calcium carbonate "oolith" concretion, typical of Jurassic limestones (field of view 1.6 mm), and (c) internal structure of the outer layer of a calcareous oolith, with microporous, radial calcium carbonate texture (field of view 220 µm).*

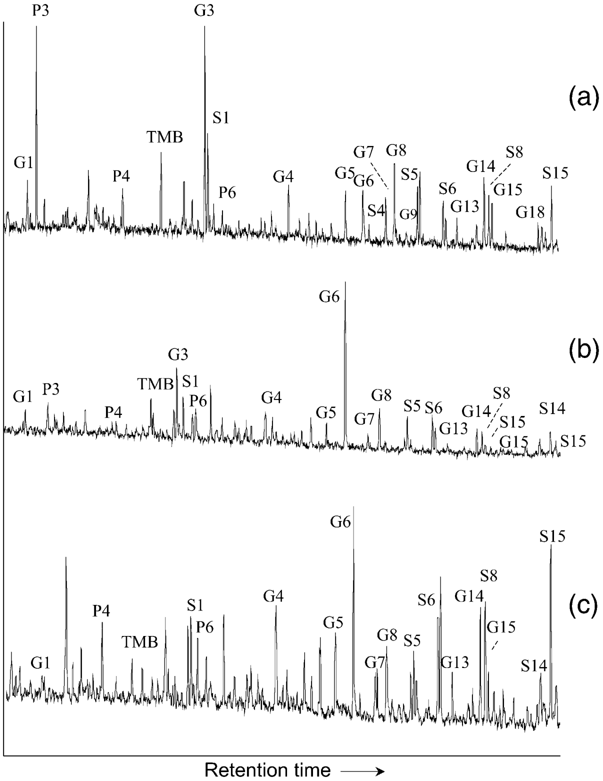

FIG. 5—*Partial chromatogram of the total ion current (TIC) for the tetramethylammonium hydroxide (TMAH) thermochemolysis products from sample sites (a) 1, (b) 2, and (c) 3. Individual compound structures are given in Fig. 6.*

to a site where local vegetation is dominated by agricultural grasses. They were not successful in identifying proximity to a major industrial works. Where interpretations of components were common to experts analyzing the mineralogical and organic components of the sample respectively, there was broad agreement in terms of their interpretations, which were all mutually compatible.

Site 2—Domestic Garden, West Bridgford, Nottingham: Mudstone (See Table 3)

The positive feature of the mineralogical XRD analysis was the identification of an unusual clay mineral assemblage featuring corrensite, which is only known to occur in two stratigraphical units: the Permo-Triassic Sherwood Sandstone Group and the Mercia Mudstone Group (and in the latter in one of a restricted number of formations). These two lithostratigraphical units are spatially extensive soil parent materials, extending in outcrops from northern to southern England. However, the formations referred to in the expert knowledge (52) are restricted to the Midlands and Cheshire Basin. The parent material at this site was the Edwalton Formation (Mercia Mudstone Group); hence this interpretation was of some significance. The interpretation of the mineralogical composition undertaken by the expert in SEM analysis identified the Carboniferous as a possible parent material, based on the presence of coal fragments. However, it was noted that their presence could have been due to anthropogenic activity. Collectively, the XRD observations of corrensite were acknowledged to be far more significant and the overall conclusion was that the coal was likely to be anthropogenic and the parent material either Sherwood Sandstone or Mercia Mudstone, both entirely consistent with the SEM observations indicating a siliciclastic sediment parent body.

The pollen/spores and organic matter signature results and interpretations both correctly interpreted the presence of hardwood (e.g., ash, beech, hazel), tree pollen, and lignin components respectively. Another common feature of the interpretation was rust fungi (urediospores) in the palynomorph assemblage (identified with the assistance of another forensic palynologist—Dr. Patricia Wiltshire) and the inferred presence of fungi through the oxidative alteration of lignin. The pollen/spore assemblage identified a broad range of plant types including herbs, ferns, and

TABLE 3—*Summary of the four independent expert analyses: Site 2–domestic garden, West Bridgford, Nottingham.*

Method	Results	Expert Interpretation
XRD+optical microscopy	Poorly sorted, medium-brown clayey silty sand. Abundant coarse-grained lithic/anthropogenic clasts minor amounts of organic material. Whole rock analysis dominated by quartz (*c.* 71%) with feldspar (*c.* 18%), "mica," chlorite, calcite, hematite (Fig. 6*a*). Clay mineral assemblage features major corrensite and illite with minor chlorite and kaolinite (Fig. 6*b*)	Appearance and bulk mineralogy suggest an interbedded mudstone/sandstone parent. Corrensite suggests that the parent material was Permo-Triassic. Significant anthropogenic input. Likely provenance: made-ground possibly developed from a Sherwood Sandstone Group or Mercia Mudstone Group (Gunthorpe, Edwalton or Cropwell Bishop formations) parent
SEM	Minor organic component: woody stems and moss. Mineral component: silty quartz sand with rare monocrystalline quartz gravel. Piece of micaceous siltstone. Unusual particles: coal/soot fragments, plastic, brick, scaly fibers, iron, and steel. (see Fig. 7)	Parent body is siliciclastic and includes siltstone, sandstone, and grit. Possibly Millstone Grit or other Carboniferous formation, especially if coal fragments are *in situ*. Abundant anthropogenics suggest current or recent domestic or low-grade industrial activity
Palynology	The fine organics comprise plant tissues and pollen/spores. The urediospores of rust fungi (Uredinales) are the most abundant palynomorph. Pteridophyte spores, tree pollen, shrub, and herb pollen and Carboniferous spores are also present. Rare diatoms were also observed. The coarse organic fraction is dominated by plant debris and mineral/rock fragments. Rare brick, glass, and slag fragments are also present	The dominance of urediospores indicates the probable infection of garden grasses by rust fungi. Fungal material, such as hyphae, is abundant and represents degradation processes typical of a bioactive garden soil. The other palynomorphs comprise herbs, pteridophytes, shrubs, and trees consistent with a garden setting. Rare diatoms were derived from a local source of freshwater. The Carboniferous spores are interpreted as having been derived from domestic coal incorporated into the soil
Organic matter	Fig. 5*b* S/G 0.37 C/G 0.08 $(Ad/Al)_G$ 3.5 $(Ad/Al)_S$ 2.5 Γ 15.0	Lignin signature is from an angiosperm wood (hardwood) such as beech oak or ash. The lignin fraction of the hardwood has been subject to soft-rot or white rot-fungal decomposition (rotted)

XRD, X-ray diffraction; SEM, scanning electron microscopy.

mosses, and was interpreted as being consistent with a mixed garden setting.

Diatoms were observed; these were probably derived primarily from the soil. Alternatively, their presence is possibly related to a raised bird water bath in the garden, the diatoms having been somehow dispersed over the soil below. Spores of Carboniferous age were identified and were assumed to have been derived from the soil; the same interpretation inferred above. However, as these spores could not be derived from this soil parent material, it is most likely that these spores were derived following the use of domestic coal that has been incorporated into garden soil. In the built environment, the occurrence of these robust spore types could commonly lead to erroneous interpretations.

The organic matter signatures and pollen/spore assemblage were collectively interpreted as being consistent with a garden setting, because of evidence of intensive fungal activity borne out by the oxidized state of the lignin and abundant urediospores, indicative of fungal decay. Three of the experts made reference to common anthropogenic material in the soil sample, which is also compatible with a garden setting.

In summary, the independent evidence for the identification of the parent material type was equivocal. Although, clay mineralogical XRD analyses correctly identified the parent material to formational level and thereby restricted the provenance of the sample, the presence of coal fragments and Carboniferous spores led to erroneous inferences by these experts. However, when a collective interpretation was made, it became clear that the evidence implicating the Carboniferous was more likely to have come from anthropogenic coal and so the XRD data indicating the Permo-Triassic was accepted as being a more reliable indicator of parent geology. The pollen assemblage and lignin signatures effectively identified the dominant vegetation and a garden setting was inferred. In contrast to site 1, it would have been difficult to provide any local constraints on the provenance of the sample material that would have been of practical benefit as this type of locality (domestic garden setting) is common.

Site 3—Wollaton Park, Nottingham: Sandstone, Siltstone, Mudstone (Table 4)

The mineralogical experts (XRD and SEM) positively identified that this soil had developed from a parent material of Carboniferous or Jurassic age. The SEM analysis identified coal fragments indicative of coal-bearing strata, which constrains the lithostratigraphy to the Carboniferous Coal Measures. The formation underlying the site is the Pennine Middle Coal Measures Formation. It is noteworthy that the palynologist interpreted the presence of Carboniferous spores as providing evidence of a Coal Measures parent material. The SEM analysis identified the precipitation of pyrite, gypsum, and halite, and inferred that this was related to evaporation of a freshwater body (a lake or pond) in an organic-rich environment. The identification of a single zinc-oxide particle was interpreted as evidence of former industrial activity, but no broader interpretation was placed upon it (Fig. 9a).

The results and interpretation of the organic matter analyses were consistent with the findings of the other analyses. The organic matter lignin signatures identified a complex distribution of products and interpreted these as multiple sources of lignin from woody and non-woody angiosperm plants such as oak trees and grass. Likewise, the pollen/spore assemblage contained abundant tree pollen (dominated by alder, with lesser amounts of pine and oak), implying a local densely wooded area. The presence of diatoms and the alga *Pediastrum* provided further evidence of a freshwater, lacustrine environment.

In combination, these independent interpretations constrained the provenance of the sample to four large regions of England with outcrops of Carboniferous Coal Measures. Furthermore, the Coal Measures parent material and proximity to an evaporative freshwater environment and local alder-dominated woodland limited further the provenance of the sample. The organic matter signatures provided detail on the depositional environment, while the pollen would have been deposited by wind. It is noteworthy

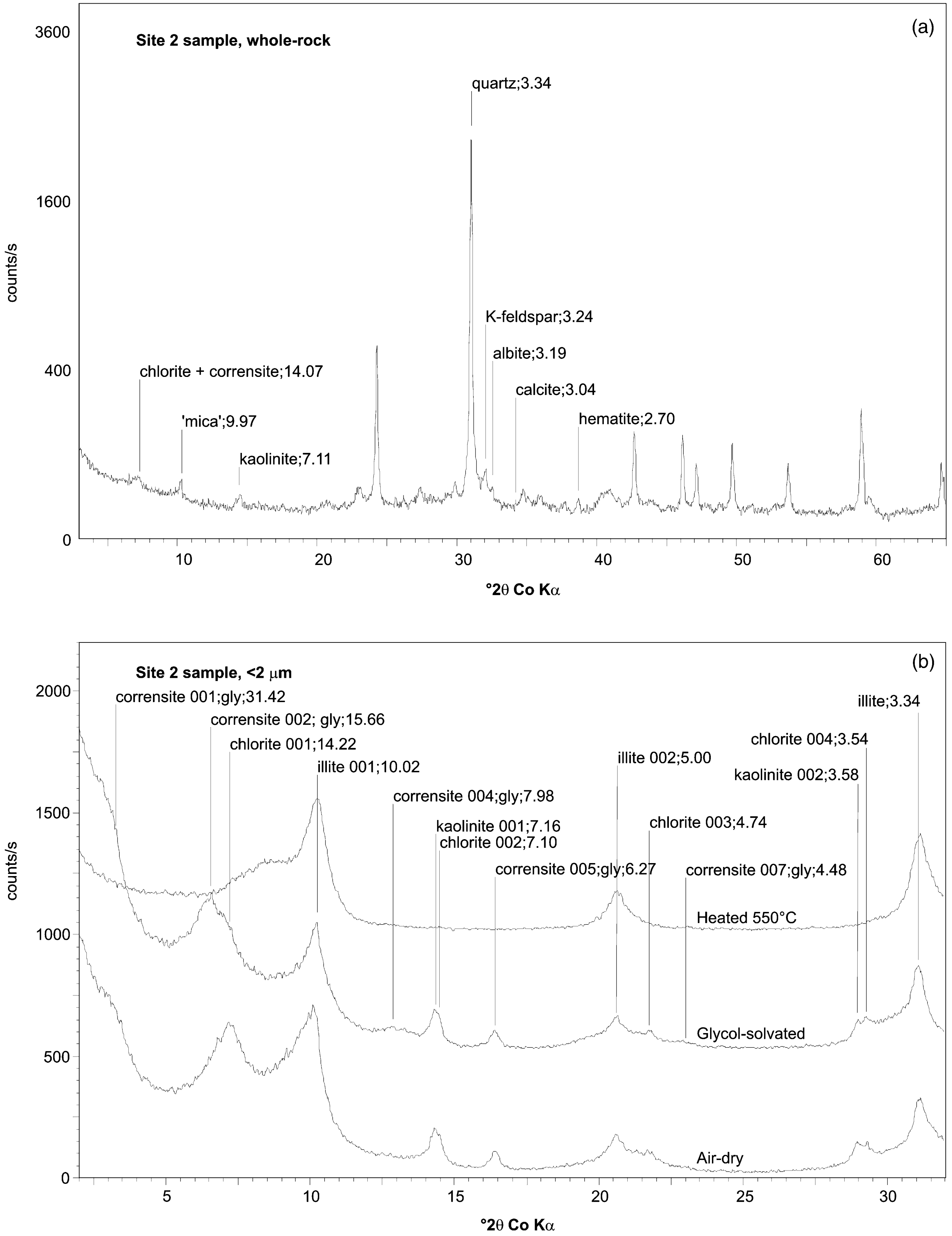

FIG. 6—*X-ray diffraction traces for site 2 sample (a) whole-rock trace, mineral phases are labeled with their most intense/diagnostic peak and corresponding d (Å) spacing (b) air-dry, glycol-solvated and heated 550°C <2 μm traces, diagnostic clay mineral 00l basal spacings are specified with their d (Å) spacing.*

FIG. 7—*Scanning electron microscopy image of sample from site 2: gravel-sized particle of siltstone (field of view 670* µ*m).*

that the lake sediment provided an ideal environment for the preservation of organic material.

Discussion

On the basis of assessing samples from only three sites it would be unwise to draw broad conclusions. However, we believe certain features of our findings are worthy of comment. It is clear that our study was most successful in constraining sample provenance at those sites with distinctive mineralogical or vegetative properties, and this is clearly a predictable outcome. In the cases we presented, some lines of evidence were shown to constrain the regional or environmental location effectively. These include: the mineralogy of a Jurassic ironstone parent material for site 1; XRD identification of the unusual mineral corrensite, from the Mercia Mudstone Group at site 2; the mineral and organic features associated with a stagnant water body at site 3 (gypsum, halite, and diatoms). By contrast, the pollen/spore assemblage of the domestic garden proved difficult to interpret with any confidence. Furthermore, some lines of evidence proved to be potentially misleading; most significantly the presence of Carboniferous coal fragments and allochthonous spores were falsely thought to be derived from the parent geology at site 2. When multiple lines of evidence were combined, this led to far more robust interpretations regarding provenance. We conclude therefore that the combination of environmental properties of natural, earth-derived samples across the landscape give rise to a wide range of diagnostic potential in terms of constraining provenance. It is important to note that in our case study we adopted a best-case scenario; we had greater quantities of sample material available for analysis than would normally be the case in most forensic investigations. However, the experts analyzed the samples without any prior knowledge of their provenance. Such a situation is rarely the case in forensic investigations. Similarly most investigations involve matching samples from a crime scene to samples taken from a person or object. In such investigations, far more background information is available and investigators are likely to be more successful than in the blind provenance study outlined here.

The use of SEM did not identify many diverse, anthropogenic particles in the samples, which before the study we had expected to be a potentially significant means of providing information on provenance. The probable reason for this is that these particles tend to be small and diluted by the natural soil component. In order to identify this population by SEM, a specific and systematic inspection routine ought to be employed in which the imaging controls are used to maximize the visibility of small, "heavy" particles. As this was a "blind" test case, the method adopted was to carry out a brief and general examination of the samples. If heavy anthropogenic particles were expected to be present

TABLE 4—*Summary of the four independent expert analyses: Site 3–Wollaton Park, Nottingham.*

Method	Results	Expert Interpretation
XRD+optical microscopy	Well-sorted, dark brown sand with abundant organic material and prismatic gypsum crystals. Quartz dominates the whole rock analysis with minor feldspar and gypsum and traces of chlorite, calcite, "mica," and hematite (Fig. 8*a*). The clay mineral assemblage is composed of major illite and kaolinite, minor chlorite, and a trace of illite/smectite (Fig. 8*b*)	Appearance and bulk mineralogy suggest a quartz-rich sandstone parent. Gypsum may suggest anthropogenic input or pyrite oxidation. The clay mineral assemblage suggests that the parent material was unlikely to be younger than Cretaceous, or Lower Palaeozoic or Permo-Triassic. Likely provenance: a wooded soil possibly developed from a Carboniferous or Jurassic sandstone
SEM	Abundant organic component: stems, leaves, bark, seeds. Mineral component: mostly unstained quartz sand. Unusual particles: diatom, calcareous shell fragment, Zn oxide. Recent surface precipitates: halite, gypsum, Fe sulphide (Figs. 9*a–c*)	Organics suggest woodland. Precipitates and diatom strongly suggest soil is close to or beneath lake or pond. Parent is likely to be siliciclastic sandstone, possibly Carboniferous if coal is *in situ*. Zinc oxide particle implies possible industrial activity
Palynology	The sample is organic-rich and yielded alder pollen and plant tissues. Pollen of other trees, dwarf shrubs and herbs, fern spores, Carboniferous spores, diatoms, and *Pediastrum*, were also observed. The coarse organics are dominated by herbaceous material largely leaf fragments. Sand, pebbles, humic material, and insect debris are common. A fragment of a mollusc shell was observed	The occurrence of diatoms, *Pediastrum*, the mollusc shell, and the organic richness, indicates that the sample is a lake sediment. The subaqueous nature of this material would have inhibited decomposition and winnowing of the abundant leaf debris. The common herbaceous material and tree pollen strongly suggests proximity to a wooded area dominated by alder. The bedrock of this area is Westphalian (Carboniferous), due to the presence of spores of this age, sandstone, and coal
Organic matter	Fig. 5*c* S/G 0.56 C/G 0.07 (Ad/Al)G 1.6 (Ad/Al)S 6.5 Γ 1.4	Lignin signature indicates a multiple sources of lignin from woody and non-woody angiosperm plants

XRD, X-ray diffraction; SEM, scanning electron microscopy.

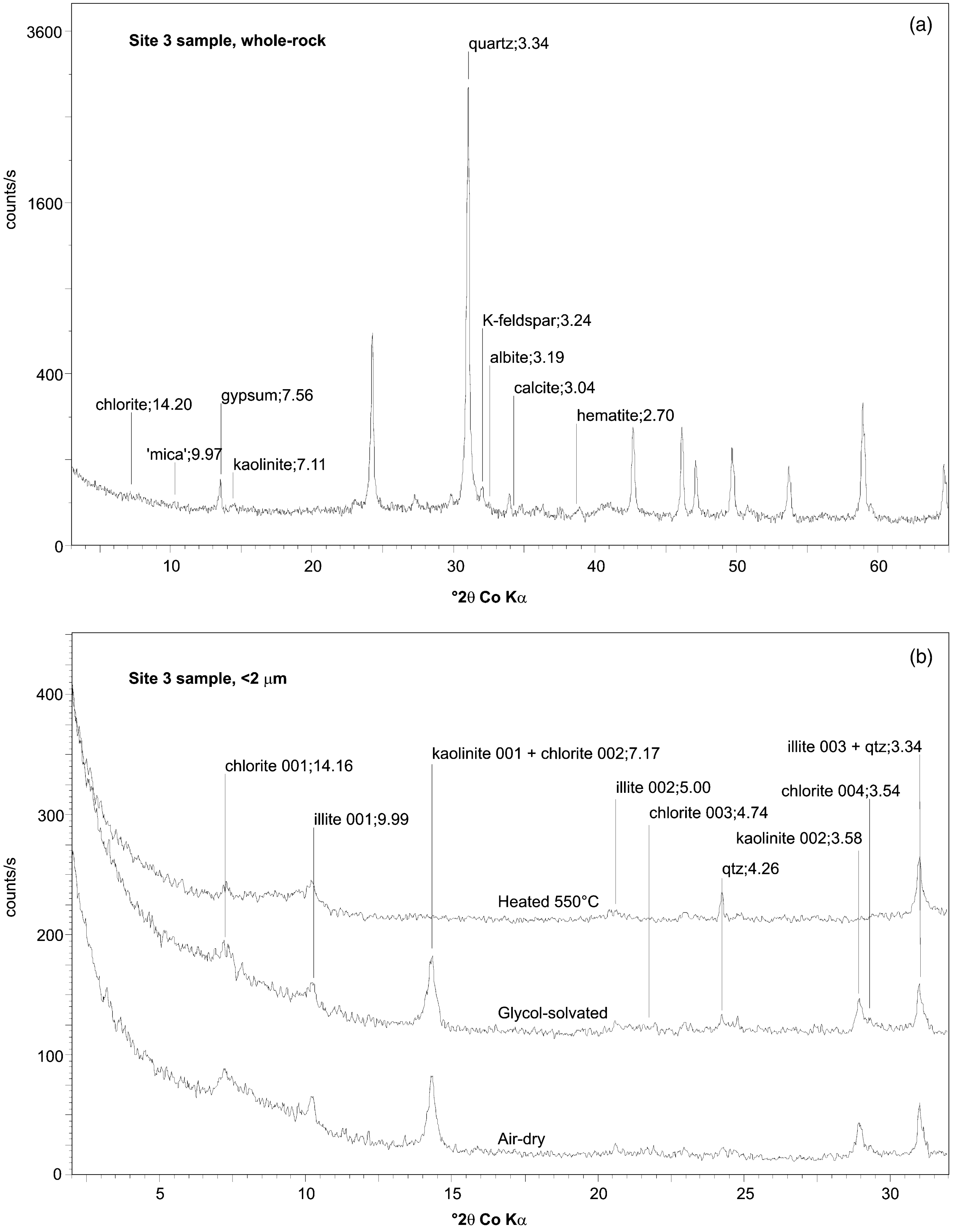

FIG. 8—*X-ray diffraction traces for site 3 sample (a) whole-rock trace, mineral phases are labeled with their most intense/diagnostic peak and corresponding d (Å) spacing (b) air-dry, glycol-solvated and heated 550°C <2 μm traces, diagnostic clay mineral 00l basal spacings are specified with their d (Å) spacing.*

for some reason, a specific search routine could be established. Instead, the most commonly observed anthropogenic particles were fragments of coal and soot. Following the widespread use of coal for domestic heating throughout the majority of England over the last few centuries, its widespread dispersal is to be expected, and its diagnostic power may be of limited value.

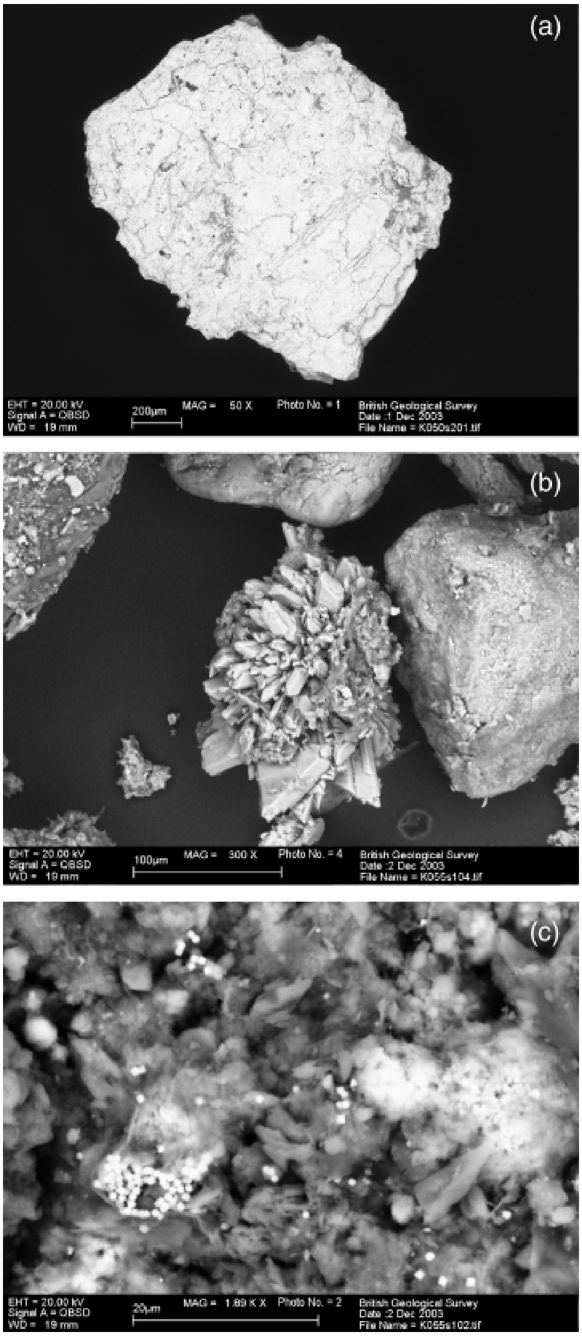

FIG. 9—*Scanning electron microscopy images from site 3: (a) zinc oxide particle (field of view 2.4 mm), (b) calcium sulphate (gypsum) crystals, recently nucleated on a soil particle (field of view 390 µm), and (c) iron sulphide "framboids"—small bright spherical to cubic features (field of view 62 µm).*

Any interpretation of sample provenance based on the presence of coal or soot fragments should be treated with caution.

This study has demonstrated that combining four techniques in the identification of soil minerals and local plant communities was very effective in providing information on the provenance of earth-derived material for two out of the three sites studied. At the other site, although the mineralogical analysis correctly identified the parent material to the level of the geological formation, difficulties were encountered in providing more local site information regarding the domestic garden setting. The identification of mineralogical assemblages by XRD analysis demonstrated the value of this technique, correctly identifying each parent material.

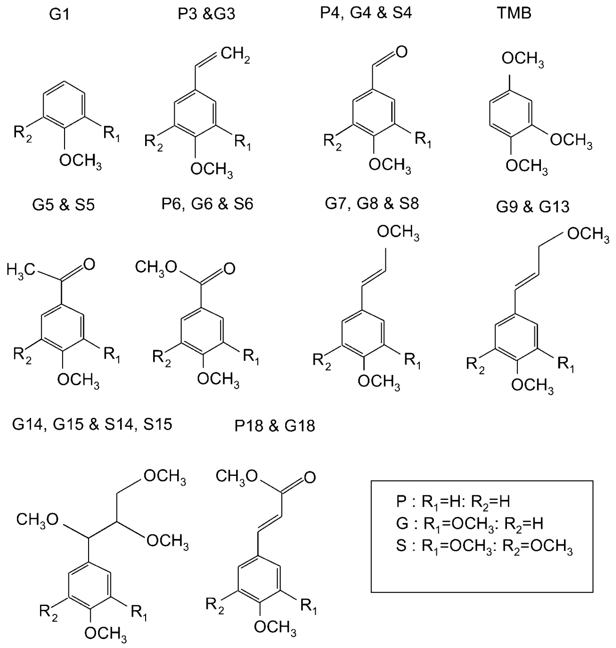

FIG. 10—*Structures of tetramethylammonium hydroxide thermochemolysis products from forensic soils; compound numbers refer to peaks in Fig. 5.*

Clay mineralogy has the potential to identify specific stratigraphic formations and/or geographic locations, particularly in a country with a diversity of distinctive parent material types.

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