Potential and pitfalls in establishing the provenance of earth-related samples in forensic investigations

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Short running header: the provenance of earth-related samples

Abstract

Establishing the provenance of mud, soil or other earth-derived particles found on items such as clothing, footwear or vehicles, can make a significant contribution to the intelligence and evidential phases of a forensic investigation. This paper reports the findings of a blind test case in which four experts in mineralogy, environmental particles, palynology and structural characterisation of organic matter at the molecular level were asked to provide information on the provenance of three soil samples from widely differing sites.

The study demonstrated that combining multiple techniques and expert interpretations was very effective in the assessment of provenance for two out of the three study sites. At the other site, although the mineralogical analysis correctly identified the parent material to the level of the geological formation, some other lines of evidence proved to be potentially misleading. Clay mineralogy demonstrated a powerful potential to identify specific stratigraphic formations.

Keywords: 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).

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 (2). 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 (3). 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.

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. Due to financial constraints, investigators may often choose to focus on one or two of these components. 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 analysing 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, whilst 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.

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 sub-samples were then provided to experts in X-ray diffraction, scanning electron microscopy, 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 analysed. 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 Figure 1.

The samples for the study were all collected in October 2003. At each site, clean boots were worn and used to walk repeatedly across a small patch of ground. Around 20 g of a forensic sample of soil or sediment was brushed 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 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 analyse.

Background to the methods, sample treatment and analytical procedures

X-ray diffraction

Since the early 1990's, X-ray powder diffraction (XRD) has proved to be a highly effective tool for the forensic mineralogist (3-9). 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 employed in the identification of 'contact traces' from a wide variety of materials (5). Analyses may be required to identify a single substance (10, 11) or to compare two samples to ascertain whether they have a common source (3, 4). Importantly, XRD analysis is able to provide reliable data from small (<10 µg) specimens recovered from crime scenes and suspects. The non-destructive 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 (12). Due 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 (3, 13, 14)

Recent advances in quantitative XRD analysis have extended the applicability of the technique to provide statistical reliability in similar rocks and soils (4). 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 (15) 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 ±2.5% for concentrations >60 wt%, ±5% for concentrations between 60 and 30 wt%, ±10% for concentrations between 30 and 10 wt%, ±20% for concentrations between 10 and 3 wt% and ±40% for concentrations <3 wt% (16).

The three forensic samples 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 approximately <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 µm. To ensure a finer and uniform particle-size for whole-rock XRD analysis, the powders were then wet micronised under acetone in a McCrone micronising mill for 10 minutes. The resulting slurries were dried, disaggregated and then back-loaded into standard aluminium sample holders. XRD analyses were carried out using a Philips

PW1700 series automatic diffractometer equipped with a cobalt target X-ray tube and operating at 45 kV and 40 mA. Diffraction data were analysed 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 3-65 °2θ at a scanning speed of 0.8 °2θ/minute. 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 deionised water using a combination of reciprocal shaking and ultrasound treatment. The resulting dispersion was then sieved to <63 µm and the material placed in a 100 ml measuring cylinder with 0.5 ml 0.1M 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. *c.*15 mg of the dried <2 µm material was then Ca-saturated using 1M $CaCl_2.6H_2O$ solution. To achieve full saturation, the solution was replaced three times with fresh $CaCl_2$ and the material then washed with deionised water to remove all traces of reagent. The material was then re-suspended 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 2-32 °2θ also at 0.6 °2θ/minute after airdrying, ethylene glycol-solvation and heating to 550°C for 2 hours. 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.

Scanning electron microscopy (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 characterise grain surface textures, surface coatings and diagenetic features (17). 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 (18). 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 (19, 20).

SEM techniques have been extensively used in forensic science (21, 22) and in some cases have become standard, for example in the analysis of gunshot residue (23). SEM has been applied to forensic soil analysis in numerous legal cases and a small amount of research and case material has been published (19, 20, 24-26). Whilst 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 (20, 25).

Firstly, a visual inspection of the samples was carried out with the aid of a x10 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 aluminium 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 Scanning Electron Microscope operated at 20 KeV under ‘variable pressure’ conditions. Conventional SEM requires the sample chamber to be kept under high vacuum conditions such that non-conducting 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 non-destructive 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. The latter mode can be used to search for high atomic density material such as anthropogenic heavy metal particles indicative of industrial processes. 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 (27). 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 (28-30). 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 (29, 31). Thermochemolysis with TMAH effectively depolymerises the lignin macromolecule into small fragments by cleaving propyl-aryl ether bonds and methylates hydroxyl groups located on aromatic rings and alkyl side chains (32).

The procedure is ideally suited to forensic analysis of soil organic matter since it requires only 0.5-5 mg of sample yet provides specific information at the molecular level on lignin (33-35). 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) (36) 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 characterise 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 (33). Increases in the relative intensity of phenolic acids to aldehydes are indicative of oxidative fungal decay which provide a further chemical descriptor for correlation purposes (37, 38).

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 prior to 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 Gas Chromatography (GC) using a fused silica VF-5ms column (60m length x 0.32 mm i.d. x 0.25 µm film thickness). The GC oven was operated using the following program; isothermal for 5 minutes at 40 °C; then raised from 40 °C to 300 °C at 4 °C per minute and held isothermally at 300 °C for 10 minutes 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 (39, 40). 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 sub-fossil and modern sediments. There is an extensive literature on the environmental interpretation of Quaternary pollen (41-43). 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 USA (3, 44-48). A comprehensive account of the problems inherent in forensic palynology has been published by Mildenhall (47).

The palynology of each of the three samples in this study was investigated in order to characterise 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 (49). This technique deflocculates clay using sodium hexametaphosphate 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. 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 Figure 2.

Results and interpretation

Prior to 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 in Appendix A. 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 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 one kilometre 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 μm particulates from the Corus UK steelworks in Scunthorpe was 5500 tonnes between 1998 and 2002 (50). However, this steelwork emission signature becomes very diluted 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 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 analysing 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 interpretation 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 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 over a soil 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.

The results and interpretation of the organic matter analyses were consistent. 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 significantly 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 significantly constrained the provenance of the sample. The organic matter signatures provided detail on the depositional environment, whilst the pollen would have been deposited by wind. It is noteworthy 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 analysed 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 scanning electron microscopy did not identify many diverse, anthropogenic particles in the samples, which prior to 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 maximise 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 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. 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. Clay mineralogy has the potential to identify specific stratigraphic formations and/or geographic locations, particularly in a country with a diversity of distinctinve parent material types.

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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 ~~Sinemurian~~ Quartz-rich ironstone.	Agricultural field of unharvested cereals~~??wheat??~~. 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	Apple tree, holly, rhododendron, azalea, buddleia, plum tree, vibernum, pear tree, lilac, foxgloves, oxalis,

		Red-brown mudstone	pieris, grassed lawn approx. 2 m from sample site, compost heap approx. 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~~s,~~ (Duckmantian); Pennine Middle Coal Measures Formation ~~(Duckmantian)~~ Interbedded grey mudstones, siltstones and sandstones	Rhododendron/laurel (see photo 38). Alder, beech and oak trees, grass, rotting wood and leaf litter.

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 (Figure 3a). 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 (Figure 3b).	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 & rare calcareous detrital & bioclastic grains.	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.

	Coal or soot particles. Fibres. Piece of micaceous siltstone. (Figure 4a-c)	
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 fibres 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	Figure 5a S/G 0.64	Lignin signature is from non-woody angiosperm . The closest comparable plant type being from the main stems of grass

	C/G	0.25	related agricultural crops such as wheat and/or barley. The plant matter has not undergone extensive microbial alteration.
	$(Ad/Al)_G$	1.3	
	$(Ad/Al)_S$	1.2	
	Γ	0.7	

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 (Figure 6a). Clay mineral assemblage features major corrensite and illite with minor chlorite and kaolinite (Figure 6b).	Appearance and bulk mineralogy suggest an interbedded mudstone/sandstone parent. Corrensite suggests that the parent material was either Permo-Triassic or Devonian. 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.	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

	Unusual particles: coal/soot fragments, plastic, brick, scaly fibres, iron and steel. (see Figure 7)	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	Figure 5b S/G 0.37	Lignin signature is from an angiosperm wood (hardwood) such as beech oak or ash. The lignin fraction of the hardwood has

	C/G	0.08	been subject to soft-rot or white rot-fungal decomposition (rotted).
	$(Ad/Al)_G$	3.5	
	$(Ad/Al)_S$	2.5	
	Γ	15.0	

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 (Figure 8a). The clay mineral assemblage is composed of major illite and kaolinite, minor chlorite and a trace of illite/smectite (Figure 8b).	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	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

	oxide. Recent surface precipitates: halite, gypsum, Fe sulphide. (Figure 9 a-c)	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	Figure 5c S/G 0.56 C/G 0.07	Lignin signature indicates a multiple sources of lignin from woody and non-woody angiosperm plants.

(Ad/Al)G	1.6
(Ad/Al)S	6.5
Γ	1.4

Legends

Figure 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 metres of the British National Grid.

Figure 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 MPK13395.

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 MPK13396.

c *Polypodium vulgare*. This spore is from the Common Polypody fern. Site 3. Maximum dimension: 60 µm. Specimen BGS MPK13397.

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 MPK13398. e - maximum dimension: 82 µm. Specimen BGS MPK13399.

f Diatom. A silicious frustule of a pennate diatom; these types dominate freshwater/terrestrial habitats. Site 3. Maximum dimension: 93 µm. Specimen BGS MPK13400.

Figure 3. X-ray diffraction traces for site 1 sample. (a) whole-rock trace, mineral phases are labelled 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 00*l* basal spacings are specified with their d(Å) spacing.

Figure 4. SEM 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).

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

Figure 6. X-ray diffraction traces for site 2 sample. (a) whole-rock trace, mineral phases are labelled 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 00*l* basal spacings are specified with their d(Å) spacing.

Figure 7. SEM image of sample from site 2: gravel-sized particle of siltstone (field of view 670 µm).

Figure 8. X-ray diffraction traces for site 3 sample. (a) whole-rock trace, mineral phases are labelled 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 00*l* basal spacings are specified with their d(Å) spacing.

Figure 9. SEM 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).

Figure 10. Structures of TMAH thermochemolysis products from forensic soils; Compound numbers refer to peaks in Figure 5.

Appendix A – Comprehensive results and independent interpretations by each of the four experts for the three sites

Site 1 –Bratt Hill, Scunthorpe

1. X-Ray diffraction and optical microscopy

Under the optical microscope, the Site 1 sample ~~004~~ is a dry, orange/yellow-brown sand predominantly composed of well-sorted, rounded-sub angular, Fe-oxide stained, monocrystalline quartz with rare lithic grains. Very little silt- or clay-grade material was observed. A small proportion of the sample is made up of organic material that is composed of fibres, woody stems, small twigs up to 10 mm long and occasional coal fragments.

XRD analysis indicates that the whole-rock mineralogy of ~~sample 004~~the Site 1 sample is dominated by quartz (90.6%) with minor feldspar (K-feldspar, 6.3% and albite, 2.5%) and traces (<0.5%) of undifferentiated mica species (‘mica’, which may include muscovite, biotite, illite, illite/smectite etc), chlorite, kaolinite and hematite (Figure 3a).

Clay mineralogical analyses (Figure 3b) indicate an assemblage dominated by illite and kaolinite with minor illite/smectite and chlorite. Such an assemblage is not unusual in UK rocks and soils and in isolation it cannot be considered diagnostic of any single rock unit. However, assuming that the clay assemblage is representative of the bedrock underlying the soil, rather than superficial deposits and that the soil has not been transported any great distance or mixed with other sources, it is possible to make some general statements about the likely stratigraphic age of the parent rock.

During sedimentary burial, a progressive series of clay mineral reactions convert soft mud to hard, lithified mudstone and shale. Quantitatively, the most important series of reactions responsible for the lithification of mud is the progressive transformation of dioctahedral smectite to illite via a series of intermediate illite/smectite (I/S) mixed-layer minerals. Other reactions are responsible for the conversion of kaolinite to pyrophyllite and trioctahedral smectite to chlorite via smectite/chlorite intermediates. Similar reactions occur in sandstone lithologies, although these are less well constrained due to the greater degree of fluid movement during diagenesis. The progress of these reactions are usually monitored using XRD-based techniques. Since these changes are not reversed by basin inversion and uplift, they can be used to estimate maximum burial depth, particularly when combined with changes observed in organic materials as shown in the Basin Maturity Chart (51)~~(Merriman and Kemp, 1996)~~.

Using this chart, the lack of smectite in the sample, a relatively unstable clay mineral typically found in immature sedimentary rocks, suggests that the sample's parent rock has not been deeply buried and is therefore unlikely to be Cretaceous or younger in age. Similarly, the presence of illite/smectite and kaolinite, would suggest that the parent rock has not been buried to depths greater than 8 km and is therefore unlikely to be Lower

Palaeozoic or Permo-Triassic in age. The clay mineral assemblage therefore indicates that the parent material is most likely to be either Carboniferous or Jurassic in age.

Mineralogical analysis and observation therefore indicates an organic-poor soil developed on a Carboniferous or Jurassic ferruginous-sandstone parent.

2. Scanning electron microscope and petrography

An initial visual inspection showed this sample to contain a minor organic component consisting of a few woody or grassy stems and a green iridescent shell or skeletal fragment. The mineral component consists mostly of red/brown sand and very little silt, including black shiny grains which could be coal or soot particles. The sand fraction consists of well-rounded (with some angular), sub-spherical quartz grains and minor K feldspar (Plate 1). The sand grains have coatings of Fe oxide which can be thick. Fine grained phyllosilicates and Fe oxides are present, coating sand grains and forming ochreous soil aggregates (or ‘peds’). A number of large, unusual particles were identified. These include several calcareous ‘ooliths’, i.e. coarse sand-sized, subspherical, well-rounded layered concretions of calcium carbonate (Plates 2 and 3). A detrital calcium carbonate sand grain and a calcareous shell fragment were also seen. A large (2 mm) fragment of grey, micaceous siltstone or shale was identified. Lastly, some fibres were noted.

Calcareous ooliths indicate a limestone parent, and in the UK the most well-developed oolitic limestones are from the Jurassic era. However, most of the soil sediment of this sample consists of very strongly Fe oxide-stained quartz sand, suggesting a red sandstone parent. Most UK red sandstone formations are either Permian or Devonian and are not in close proximity to Jurassic oolitic limestones. One possible parent rock group which contains both these components are the Jurassic ironstones. These form a small number of very thin units (often only 6-10 m thick) which outcrop in a thin band running from North-East Yorkshire through the East Midlands and the Cotswolds to Dorset (52)~~(Simms et al., 2004)~~. ~~There are also restricted outcrops in the Hebrides (Simms et al., 2004).~~ Although most of the ooliths in these ironstones are of Fe-rich clay or other iron phases, some units also contain calcareous ooliths and/or ~~siliclastic~~siliciclastic grains, while the overlying strata may be a source of calcareous ooliths in many locations (53, 54)~~(Bennison and Wright, 1969; Rayner, 1981)~~.

3. Organic matter characterization

The TMAH thermochemolysis products of the organic matter from site 1 are shown in Figure 5a and structures presented in Figure 10. The most abundant lignin derived components were identified as 4-methoxystyrene (P3), 3,4-dimethoxystyrene (G3), 3,4,5-trimethoxybenzene (S1), and *cis* and *trans* isomers of 1-(3,4-dimethoxyphenyl)-2-methoxyethylene (G7, G8) and *threo* and *erythro* forms 1-(3,4-trimethoxy)-1,2,3-trimethoxypropane (G14, G15) as well as 1-(3,4,5-trimethoxy)-1,2,3-trimethoxypropane (S14, S15). Other important products included the cinnamyl phenols *trans*-3-(4-methoxyphenol)acrylic acid, methylester (P18) and trans-3-(3,4-dimethoxyphenol)acrylic acid, methylester which link lignin to polysaccharide via ether and ester bonds. The presence of mono, di and trimethoxylated structures confirmed that the main pool of lignin in the soil is from an angiosperm as compared to gymnosperm plant material, which would yield mainly dimethoxypehnolic thermochemolysis products derived from guaiacyl structures (55)~~(Vane et al., 2003)~~. Furthermore the high abundance of P3 and G3 as well as methylated cinnamyl components relative to other thermochemolysis products such as S4 is typical of lignin derived from non-woody angiosperm plants as compared to angiosperm woods (36)~~(Clifford et al., 1995)~~. The compositional pattern of the lignin is similar to that reported for wheat straw (*Triticum aestivum*) (37, 56, 57)~~(Vane et al., 2001a; Vane et al., 2001b); Vass, 2001) - ?? CKV to check which one of these refs should not be here??~~ . However thermochemolysis of fresh cereal crops such as wheat straw have syringyl (S) to guaiacyl (G) ratio of 1.2 and cinnamyl to guaiacyl ratio of 0.93 whereas in this current study the soil 004 had an S/G ratio of 0.64 and a C/G of 0.2 (Table 4). One plausible explanation is that the lignin component of the arable crop has been partly microbially decomposed, previous studies have shown that wheat straw decayed by the fungus *Agaricus bisporus* caused a fall in S/G ratio from 1.2 to 0.8 and a decrease in C/G from 0.5 to 0.2 via demethylation and demethoxylation reactions ~~?? check which one of these refs should be here??~~ (37, 56, 57)~~(Vane et al., 2001a; Vane et al., 2001b; Vass, 2001)~~. The ratio of phenolic derivates with acid to aldehyde containing derivatives (Ad/Al) and ratio of G6/G14+G15 (Γ) are used in tandem to asses lignin degradation state, fresh plant matter typically has Ad/Al and Γ values of ~1 where as highly decayed plant matter has Ad/Al and Γ values of 2-15 (29, 32, 55)~~(Filley et al., 1999; Vane, 2003a; Vane et al., 2003)~~. In combination, the moderate Ad/Al values of 1.3 and 1.2 and Γ of 0.69 suggest that the lignin side chains in non-woody angiosperm plant matter contained in soil 004 has not undergone extensive oxidative decay (Table 1).

4. Palynology

The fine fraction of the organic residue from this sample is moderately abundant. It is dominated by poorly-preserved, degraded plant tissue. This is interpreted as partially microbially-degraded plant material and includes some leaf cuticle. Dark wood is common and palynomorphs, which largely comprise pine pollen (*Pinus*), are relatively sparse. Insect debris (wings, carapace fragments etc.) and fungal material are both common. The fungal debris comprises fruiting bodies, hyphae and spores. The low diversity pollen flora is dominated by arboreal (tree) pollen such as alder (*Alnus*), hazel (*Corylus*), pine and spruce (*Picea*). Pine pollen is by far the most common. Pteridophyte (moss/fern) spores and herbaceous pollen are also present in low proportions. The only unequivocal herb pollen is rare chickweed (Carophyllaceae). No pre-Quaternary palynomorphs were observed, hence no interpretations of the bedrock are possible. No evidence of standing freshwater was observed.

The coarse sample fraction is dominated by broken, partially microbially-degraded cereal/grass straw and chaff. Seeds of various types are also relatively common. Dessicated humus and sand is also present in significant proportions. The sand indicates that the soil is well-drained. Certain synthetic materials are present including white fibres (?rope, bale binding or sheep wool), fragments of brick and foundry slag.

Pine and spruce pollen is capable of travelling long distances and does not necessarily indicate the presence of pine trees in the immediate vicinity. The pollen association however, indicates the presence of hazel bushes and herbs locally.

Site 2 – Domestic garden, West Bridgford, Nottingham

1. X-Ray diffraction and optical microscopy

Microscope observation of ~~sample 006~~the Site 2 sample indicates that it is composed of a dry, poorly-sorted, medium brown, clayey-silty-sand. It contains coarse-sand-sized lithic/anthropogenic clasts of clear glass, brick, red sandstone, igneous origin and blue plastic. A minor amount of the sample is made up of organic material which is composed of grasses, twigs, seed cases, acorn cups and coal fragments.

As shown in Figure 6a, XRD analysis indicates that the whole-rock mineralogy of the Site 2 sample ~~006~~ is also dominated by quartz (70.7%) but contains greater proportions of feldspar (K-feldspar, 11.6% and albite, 6.1%), ‘mica’ (7.3%), chlorite (2.3%), calcite (1.0%), hematite (0.9%) and traces of kaolinite (<0.5%).

Clay mineralogical analyses (Figure 6b) reveal an unusual assemblage of corrensite (an R1-ordered 50:50 chlorite/smectite) and illite with minor chlorite and kaolinite. Corrensite, a relatively unusual clay mineral, may form as a result of hydrothermal alteration (58)~~(Meunier, 1995)~~ but more commonly represents the diagenetic alteration of Mg-smectites and other Mg-rich minerals deposited in continental evaporite basins (16)~~(Hillier et al., 20011995)~~. In the UK, it’s distribution is very largely restricted to the Devonian of the Orcadian Basin (59)~~(Hillier, 1993)~~ and Permo-Triassic rocks of England (60)~~(Jeans, 1978)~~. In the Mercia Mudstone Group, the presence of corrensite can even be used to determine the parent stratigraphical formation ~~present~~ and geographic location as it is restricted to the Gunthorpe, Edwalton or Cropwell Bishop formations in the East Midlands (61)~~(Kemp, 1999)~~, the Upper Mudstone or Wilkesley Halite formations of the Cheshire Basin or the Upper and Lower Marl formations of Gloucestershire, Worcestershire, Warwickshire and Oxfordshire (Jeans et al., 2005).

Mineralogical testing and observation therefore indicates a made-ground soil developed on interbedded mudstones/sandstones of the Permo-Triassic Sherwood Sandstone Group or ~~the Gunthorpe, Edwalton or Cropwell Bishop~~specific formations of the Mercia Mudstone Group.

2. Scanning electron microscope and petrography

An initial visual inspection showed that this sample contains minor coarse, organic material consisting mostly of moss and woody stems. The mineral component consists of silty sand with rare, monocrystalline quartz gravel~~ (~~???~~the latter including a quartz single crystal point)~~. Some of the silt-sized grains are black and shiny and may be coal or soot fragments. On closer examination by SEM, the sand and silt grains appear to be predominantly well-rounded quartz with rare albite, K feldspar, mica and zircon. A small proportion of the quartz grains are iron oxide stained, and some are angular. Aggregates of soil material (‘peds’) are present and consist of the sand and silt with fine grained material: phyllosilicates, Fe oxides, mica and rare calcium carbonate.

Unusual particles identified include: pieces of bright blue plastic; a gravel-sized particle of micaceous siltstone (Plate 4); red brick; scaly fibres; metallic iron and tiny (<5 µm~~microns~~) Fe-Cr-Ni steel particles.

These observations indicate that the parent body is a ~~siliclastic~~siliciclastic formation including siltstones, sandstones and possibly some grit. The sample contains abundant anthropogenic particles including brick, plastic, iron and steel, suggesting an environment with current or recent human activity, possibly domestic or low-grade industrial in nature. The coal or soot fragments could be derived from the parent rock (in which case this would probably be Carboniferous) or they could be anthropogenic in origin, suggesting again human activity, either domestic or industrial. If the parent is Carboniferous, this would be consistent with the observation of gravel-sized quartz grains, which are well-represented in the Carboniferous Millstone Grit Formation.

3. Organic matter characterization

The major lignin derived thermochemolysis products from this sample were G6, S1, G4, G8, S6, G14, S14 and S15 are typical of lignin products from angiosperms (Figure ~~2b~~5b). The low abundance of P3 and G3 in this soil as compared to the first site, and presence of syringyl derivatives suggested that the main pool of plant material is derived from woody angiosperms (hardwoods). The predominance of G6 caused high $(Ad/Al)_G$ value of 3.5, this combined with a high Γ value of 15 and $(Ad/Al)_S$ value of 2.5 confirmed that the angiosperm wood contained within this sample has undergone extensive oxidative alteration such as that caused by soft or white-rot fungi. Overall the distribution of lignin thermochemolysis products in the sample is consistent with plant matter from woody angiosperms which, has undergone extensive microbial decay either prior to burial or during burial in the soil.

4. Palynology

~~?? JBRI, I think we need to say that Pat W. added to the interpretation here??~~

This soil sample produced a moderately abundant, well-preserved fine organic residue and palynoflora. The phytoclasts largely comprise abundant black wood and poorly-sorted plant tissues such as leaf cuticle. Fungal material, largely hyphae, is also abundant, higher plant pollen and spores are relatively common, and insect debris is present. Palynomorphs, largely fungal spores and various tree pollen types, proved common. The fungal spores are virtually all urediospores of Uredinales (rust fungi) and are the dominant palynomorph, representing 3097 grains per gram in this sample. These were identified by Dr P. E. J. Wiltshire. The Order Uredinales are a group of host-specific parasitic plant pathogens that affect ferns, gymnosperms and angiosperms such as grasses, and trees. Uredinales commonly infect grasses and cereals, however also affect a wide range of other herbaceous plants and frequently have a woody intermediate host such as barberry or rose. They have a complex life cycle; the urediospores are produced during the growing season. Pteridophyte (fern) spores are also common and include *Dryopteris, Laevigatosporites, Lycopodium, Polypodium vulgare* and *Sphagnum*. All these spores, and the significant numbers of heather (*Erica*) pollen, are suggestive of a damp environment. Arboreal pollen is also present with alder, birch (*Betula*), hazel, lime (*Tilia*), pine and spruce being represented. Pine pollen is the most common; the other tree pollen is indicative of nearby mixed temperate woodland. Herbs such as asters (Compositae) and enchanter's nightshade (*Circaea*) were also found in significant proportions. This indicates the occurrence of a relatively low diversity herbaceous flora. Rare diatoms also indicate the presence of a body of freshwater nearby. There is also evidence of Carboniferous input due to the presence of the spores *Calamospora* spp., *Densosporites* spp. and *Lycospora pusilla*. Species of *Densosporites* are the most common and this dominance may be due to the thick-walled, robust nature of this genus (62)~~(Wilson, 1964)~~. These forms are long-ranging within the Carboniferous, hence a detailed lithostratigraphical interpretation is not possible. However Carboniferous Limestone is an organic-lean rock type and these spores therefore indicate input from Namurian or Westphalian strata. This is consistent with the apparent presence of both ?Millstone Grit and coal in the coarse fraction (see below).

The organic ~~sample~~ fraction over 500 µm is dominated by a variety of plant debris. This comprises well-preserved leaves, bark, ?fruits, moss, seeds, seed pods and twigs. A variety of mineral/rock fragments are also common. The only synthetic elements recovered are rare brick fragments, glass and slag. The abundance of well-preserved plant material suggests damp conditions; sand is not common, implying relatively poor drainage potential.

The dominance of the urediospores of rust fungi is indicative that certain floral elements have been infected by representatives of the Uredinales. It is likely that the urediospores are from grasses in the garden. The occurrence of abundant fungal material and insect debris represents biological degradation processes in the soil. The organic residue is consistent with a highly bioactive garden or agricultural soil. However, the latter setting is less likely as the overall pollen flora is consistent with a mixed garden setting.   The non-fungal palynomorphs comprise herbs, pteridophytes, shrubs and trees.

Site 3 – Wollaton P~~p~~ark, Nottingham

1. X-Ray diffraction and optical microscopy

Under the optical microscope, the Site 3 sample ~~008~~ is composed of a wet, dark-brown sand containing abundant organic material. The sand grains are well sorted, rounded to sub-angular and composed of monocrystalline quartz. The organic material is composed of leaves (?oak), bark, twigs, seed cases and iridescent insect bodies. The dried sample also contains prismatic, 0.5 mm long gypsum crystals.

Whole-rock XRD analysis indicates a quartz-rich (85.3%) mineralogy (Figure 8a) with minor proportions of feldspar (K-feldspar, 6.4% and albite, 3.5%) and gypsum (3.5%) together with traces of chlorite (0.9%), calcite, ‘mica’, kaolinite and hematite (each <0.5%). The presence of gypsum may indicate anthropogenic input from building materials such as plaster for example, or may result from the oxidation of pyrite and reaction with Ca-rich waters.

Clay mineralogical analyses (Figure 8b) indicate an assemblage dominated by illite and kaolinite with minor chlorite and a trace of illite/smectite i.e. similar to the Site 1 sample ~~004~~.

Again using the information on the Basin Maturity Chart, the clay mineral assemblage would appear to indicate either a Carboniferous or Jurassic parent material.

The appearance and mineralogy of the Site 3 sample ~~008~~ would therefore suggest a woodland soil possibly developed on a Carboniferous or Jurassic sandstone parent rock.

2. Scanning electron microscope and petrography

The sample contains abundant large pieces of organic material, including woody stems, leaves, bark and seeds. A visual inspection of the mineral components showed them to consist mostly of unstained quartz sand with a few grains of red (iron oxide-stained) quartz sand. The very fine sand to silt size fraction included numerous shiny black grains, possibly soot or coal fragments. Analysis of the mineral components by SEM confirmed that the sand consisted mostly of coarse, well-rounded quartz grains and some ~~potassium~~ K-feldspar. Some quartz grains are multi-crystalline with minor chlorite. The fine fraction consists of mostly of phyllosilicates. Soil ‘peds’ (aggregates of particles) are present and are often rich in iron (± manganese) oxide. A siliceous diatom was seen on the surface of one of these aggregates.

Large, unusual particles include a calcium carbonate shell fragment and a 1 mm particle of zinc oxide (Plate 5). The latter was the only anthropogenic particle identified in the sub-sample.

Calcium sulphate (probably gypsum) and sodium chloride (halite) crystals have nucleated on the surfaces of some sand grains, with well-developed crystalline form and rosette-like growth patterns (see Plate 6). Fine-grained iron sulphide particles with characteristic 'framboidal' shape and size are disseminated throughout the soil sample (Plate 7). These salts and iron sulphides are all likely to have formed relatively recently, under current soil surface conditions. They are therefore indicative of the present-day chemical conditions of the soil porewaters between the grains and thus provide reliable information about the environment from which this sample was taken. Gypsum and halite salts commonly precipitate from brines or salty, stagnant waters when the water evaporates. They indicate that this soil is in some way associated with either a stagnant body of water which has recently undergone evaporation, such as a lake or pond, or some other brine source. The presence of a diatom is consistent with this environment. Iron sulphide framboids are known to form under conditions of low levels of oxygen (63). These conditions can be produced in the presence of large quantities of organic matter (which provide a food source for oxygen-consuming bacteria) and are found in lake and canal-bed sediments (64)~~(Dodd et al., 2003)~~.

Taken together, the mineralogical and petrographic observations of this sample suggest that it came from a woodland environment close to (or beneath) a body of stagnant water. The parent material is likely to be a ~~siliclastic~~siliciclastic sandstone formation. Coal and/or soot fragments suggest either anthropogenic activity or a coal-bearing parent body, i.e. Carboniferous strata. The zinc oxide particle is likely to be industrial origin but as only one was seen, it can only be tentatively suggested that this site may be, or have been, associated with industrial activity.

3. Organic matter characterization

The lignin products from this sample were identified as G1, P4, S1, P6, G4, G5, G6, G8, P18, S6, G13, S7, G14, G15 as well as S14 and S15. The presence of S and G derivatives is indicative of lignin derived from angiosperm plants as well as *p*-hydroxyphenol derivatives (P) namely P3, P4 and P6 and the cinnamyl phenols P18 and G18 which are when present with S and G derivatives indicative of nonwoody angiosperms including grass vegetation, however, this pattern is distinct from that of the proposed cereal crop (~~004~~Site 1) in that the relative abundance of P3 and G3 are lower compared to other thermochemolysis products. The most plausible explanation for this complex distribution of products is a multiple source of lignin from woody and nonwoody angiosperm plants such as oak trees and grass. Although both S and G Ad/Al values are greater than unity the moderate Γ value of 1.4 indicates only moderate microbial decomposition of lignin side chains (Table ~~1~~4).

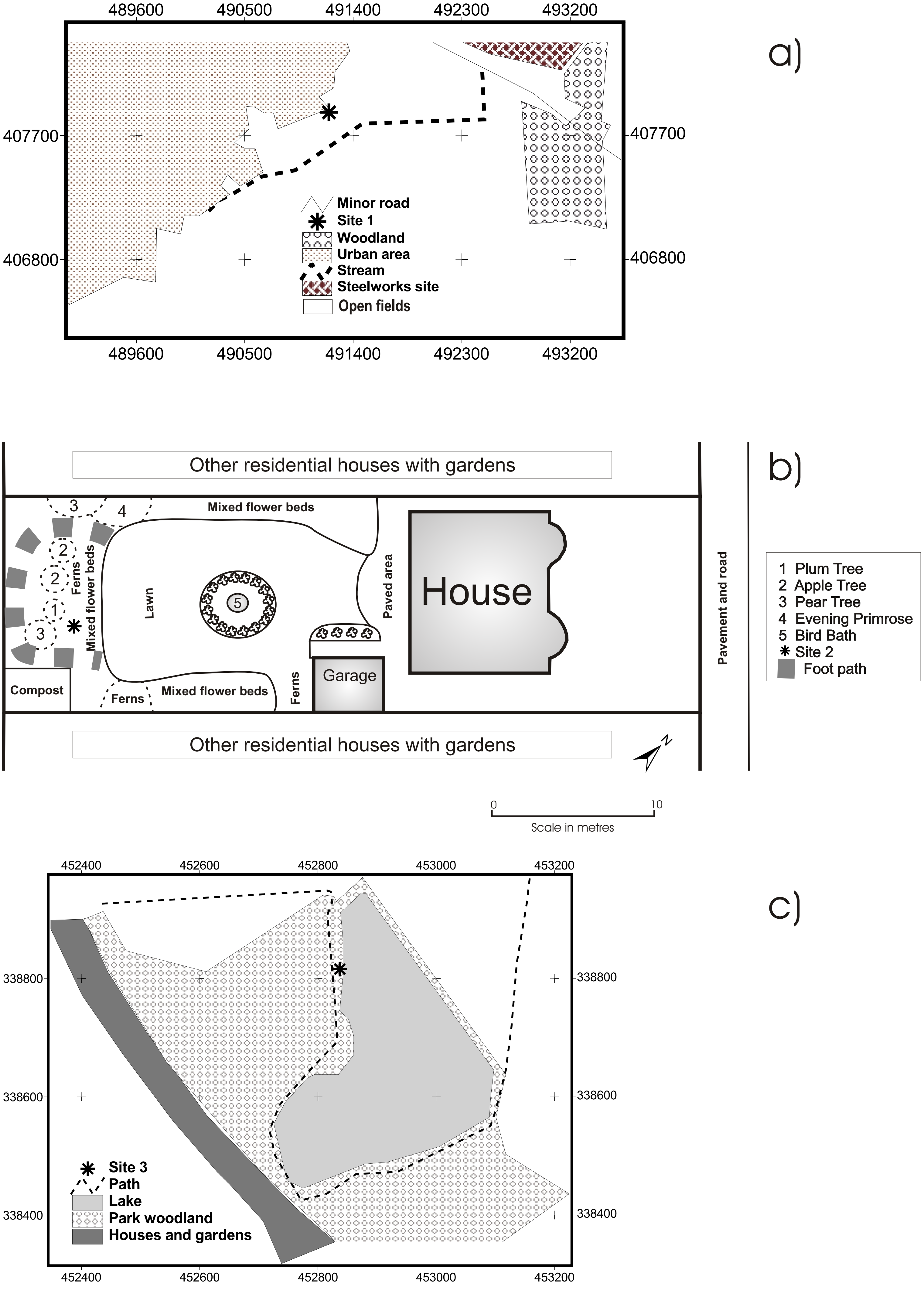
4. Palynology

This sample is highly organic-rich and produced an abundant, well-preserved palynoflora and fine-fraction kerogen association. Palynomorphs, largely tree pollen, proved abundant. The phytoclasts are dominated by varied, poorly-sorted plant tissues such as leaf cuticle. The remainder largely comprise black wood and insect debris. The palynomorphs are dominated by the arboreal genera alder, pine and oak (*Quercus*). This indicates proximity to a relatively densely wooded area populated by stands of these trees. The commonest pollen grain by far is alder, therefore this woodland is interpreted to be dominated by this tree. Smaller numbers of birch, hazel and lime pollen were also observed. Some dwarf shrub (i.e. heather) pollen were encountered, in addition to low numbers of herb pollen. The latter probably represent a sparse, weed-dominated, flora on the forest floor. Grasses are also not well represented. Pteridophytes are represented by moderate numbers of fern spores. The ferns probably grew in low, damp areas. Clear evidence of freshwater was also encountered; diatoms and *Pediastrum*, a freshwater alga, are present. These forms indicate a lacustrine setting.

The bedrock of this area is Carboniferous as moderate numbers of the Carboniferous spore *Densosporites* spp. were recorded. This genus is long-ranging within the Carboniferous, hence a detailed lithostratigraphical interpretation is not possible. However Carboniferous Limestone is an organic-lean rock type and the presence of sandstone and coal in the coarse fraction means that the bedrock is interpreted as being Westphalian (Coal Measures).

This sample is extremely rich in coarse (>500 µm) organic material. This fraction is overwhelmingly dominated by herbaceous material comprising cones, bark, buds, ?fruits, leaves, seeds, seed pods, twigs and wood fragments. Leaves and leaf fragments are the dominant constituent. Whole and partial oak leaves were observed, however other taxa are also clearly present. The sample also contains significant levels of rock/mineral material. Rare fragments that may be coal were also observed. Humic material and insect debris is present in significant proportions. A single fragment of a mollusc shell was also encountered.

The occurrence of diatoms and *Pediastrum,* the mollusc shell fragment and the overall organic-richness, indicates that the sample is from a lake or pond. *Pediastrum* is a freshwater alga that thrives in lakes and large ponds (65)~~(Batten, 1996)~~. The subaqueous nature of this material would have inhibited decomposition and winnowing of the leaf debris and promoted a build-up of leaf-mould. The presence of significant levels of insect debris is consistent with this interpretation.



Rawlins et al
Figure 1

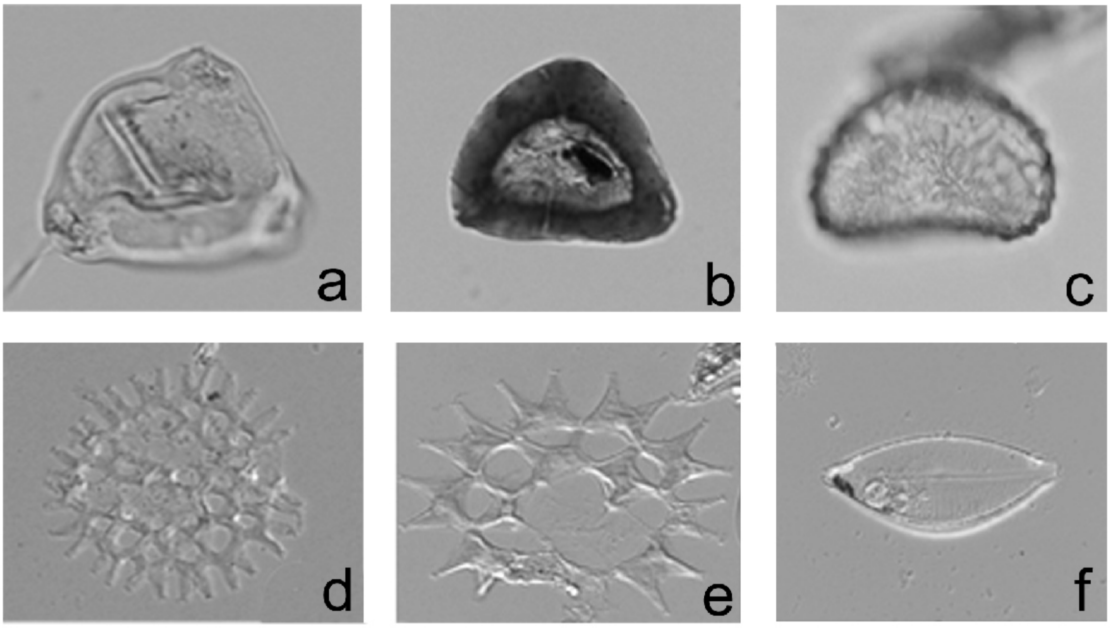


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Figure 2

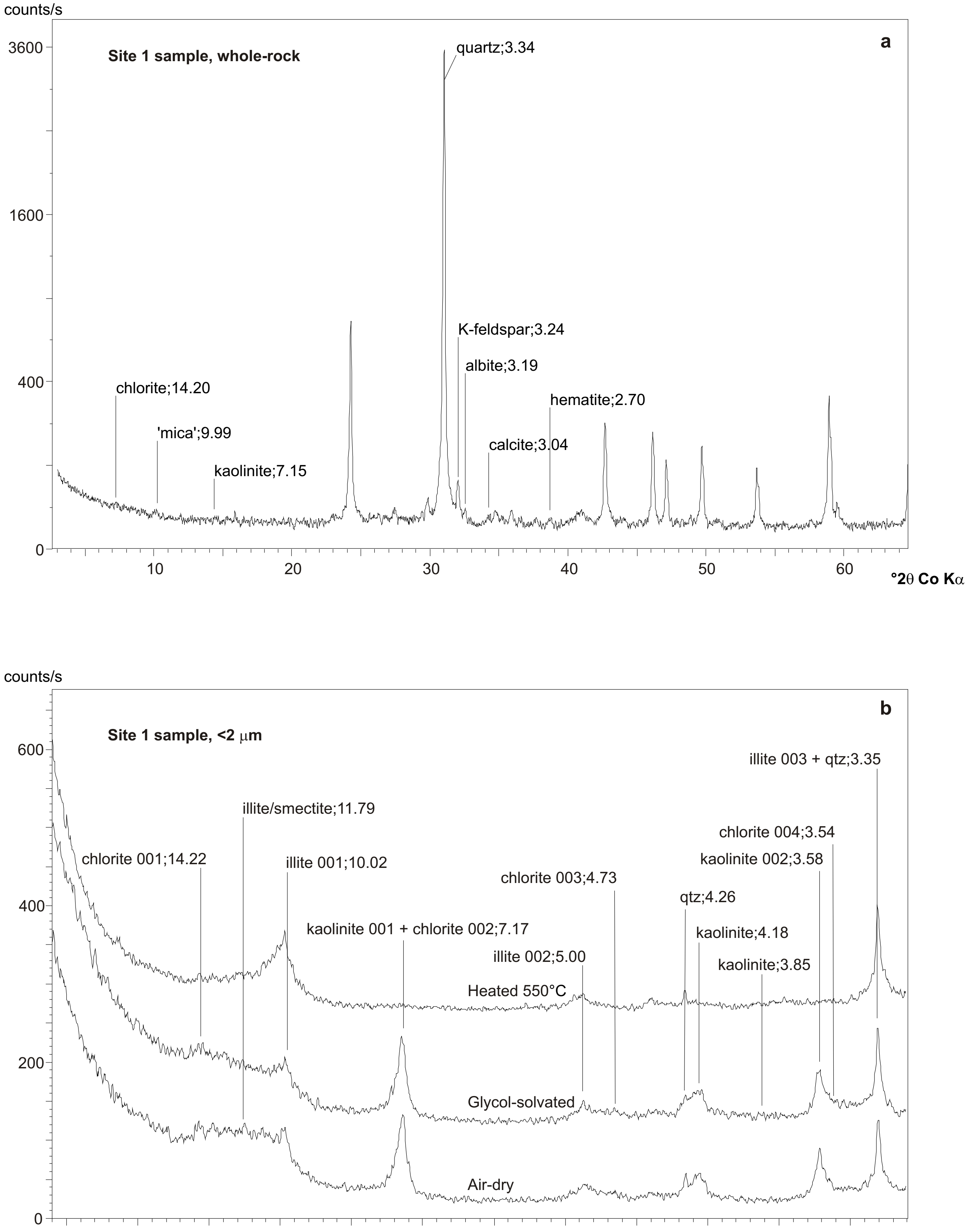

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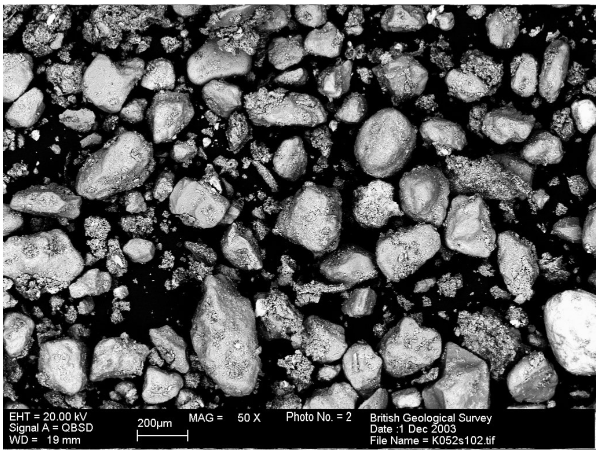
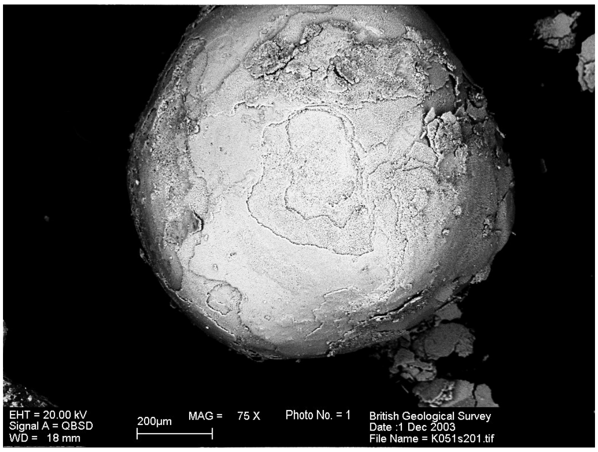
Figure 3



a)



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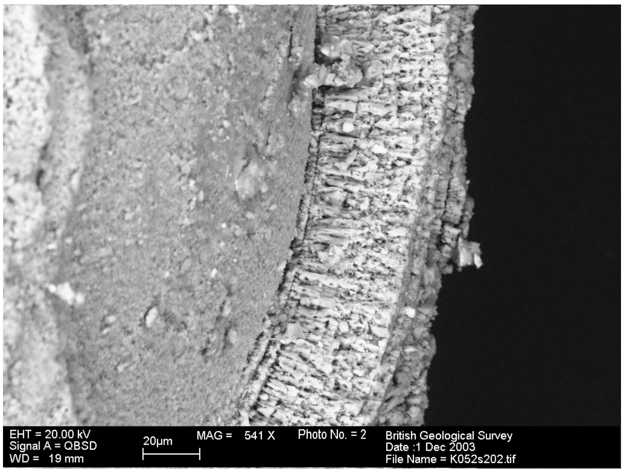

c)

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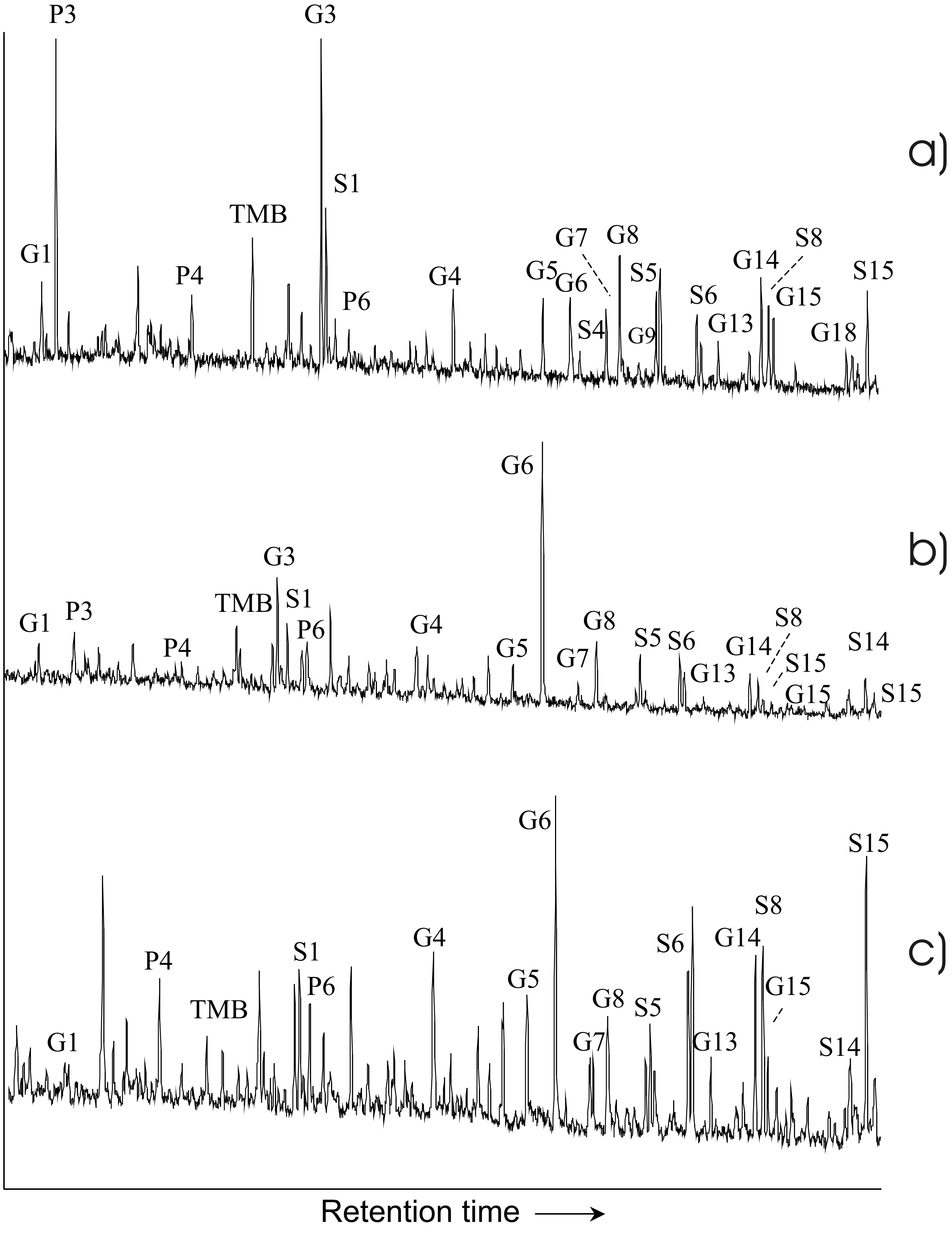
Figure 4



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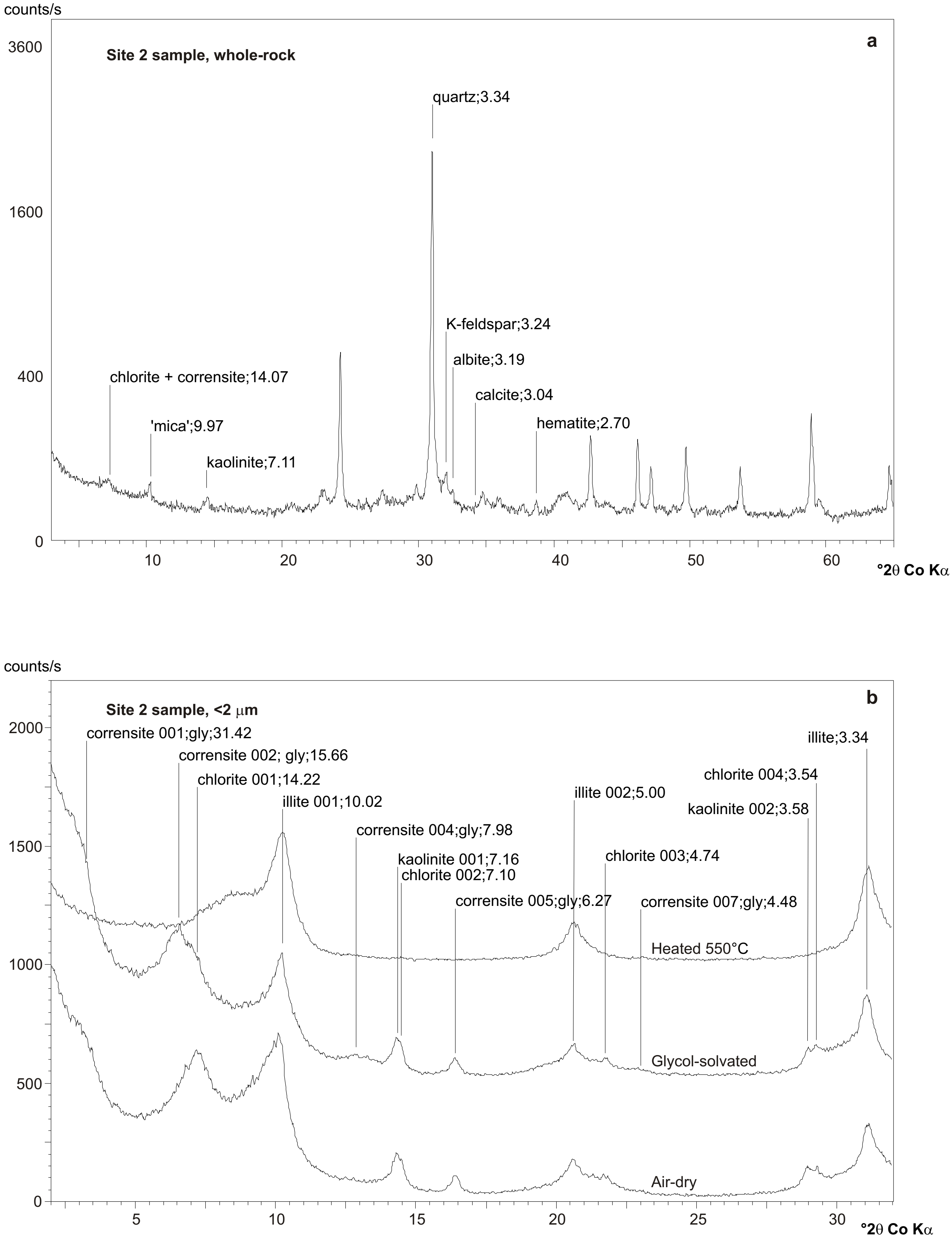

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Figure 6

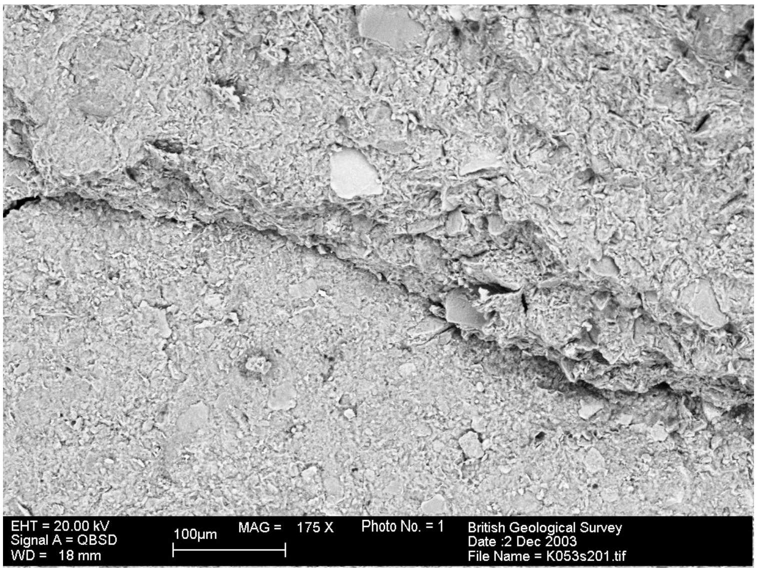

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Figure 7

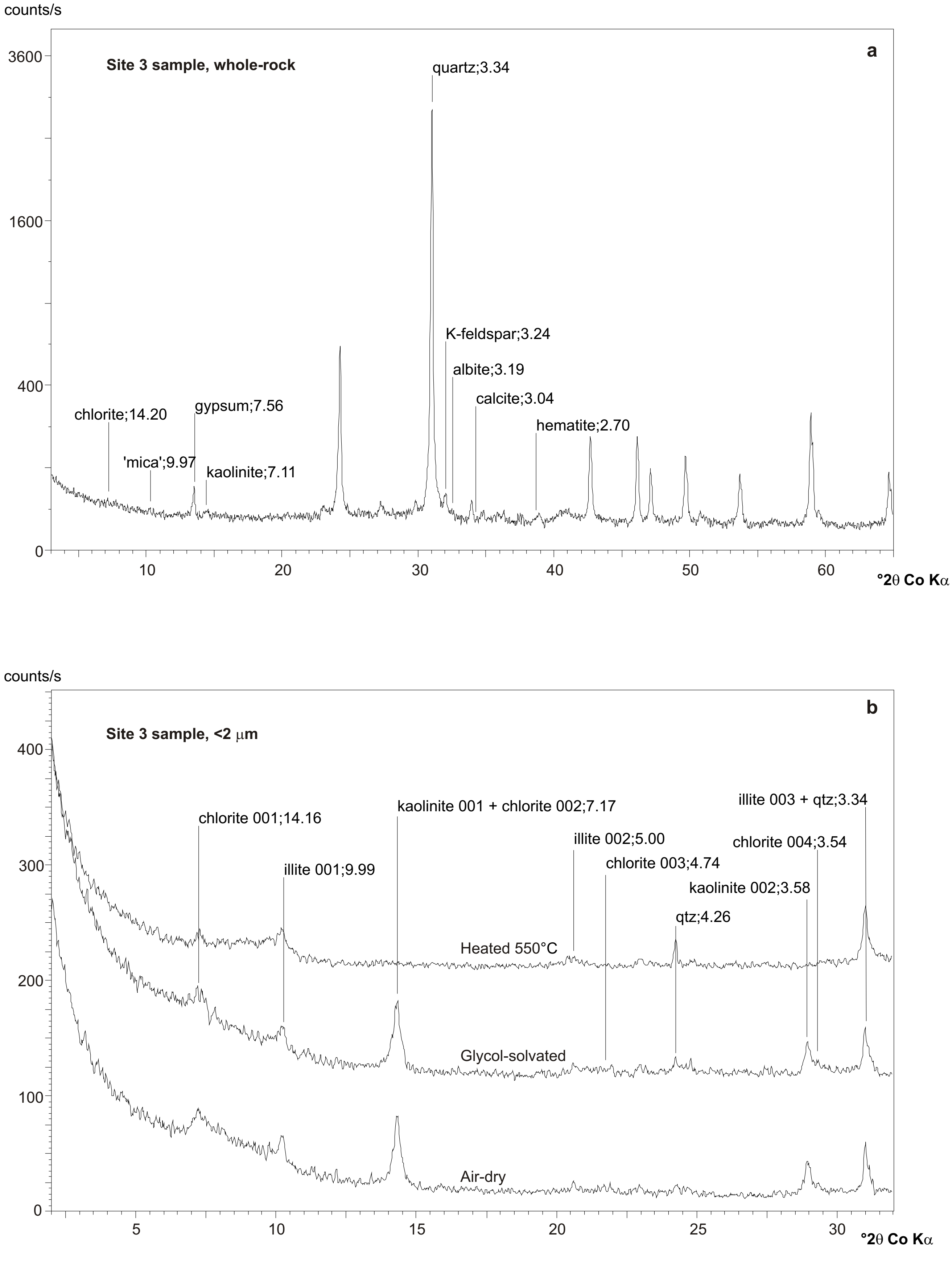

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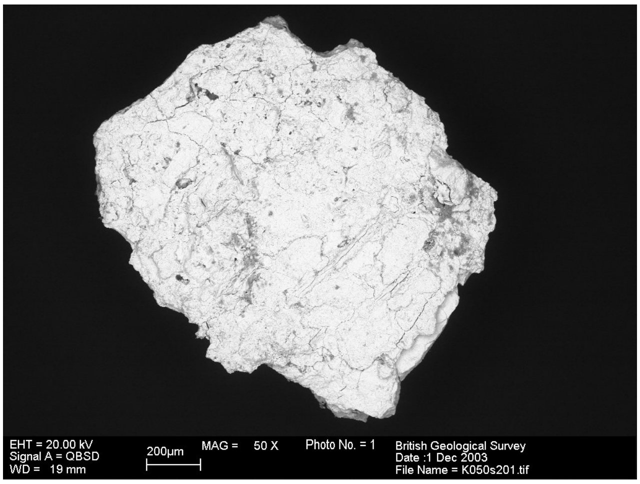
Figure 8



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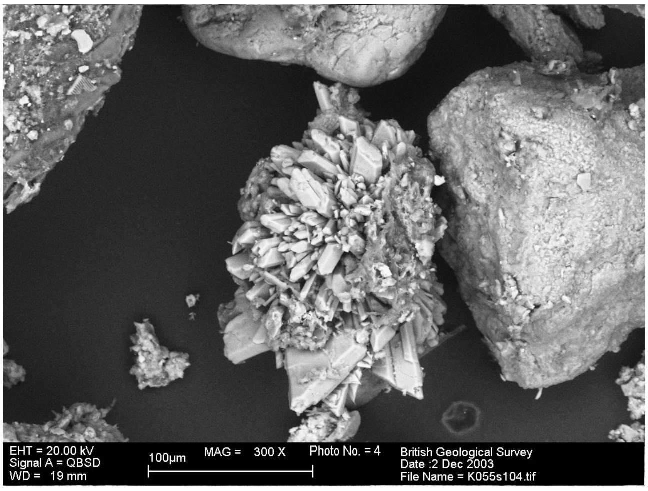

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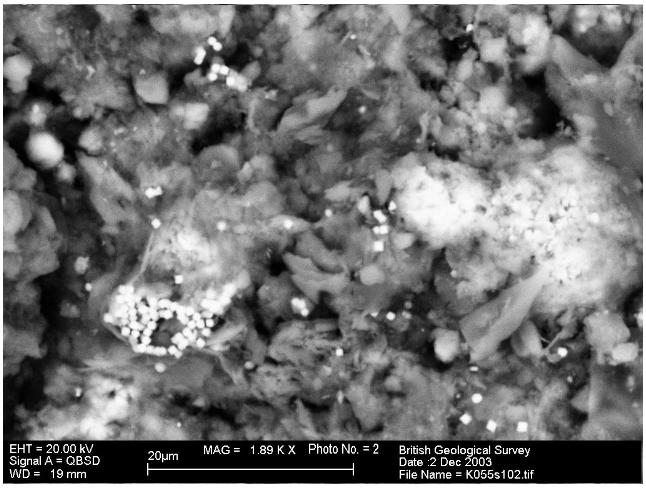
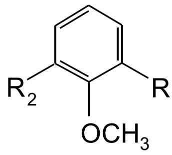


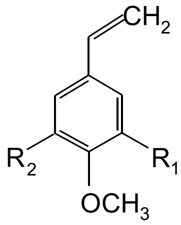
c)

Rawlins et al
Figure 9

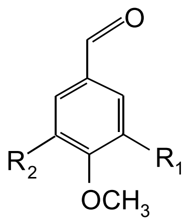
G1



P3 &G3



P4, G4 & S4



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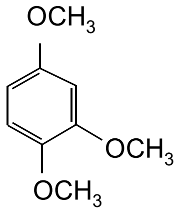
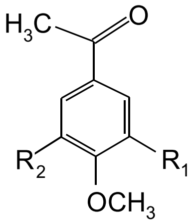
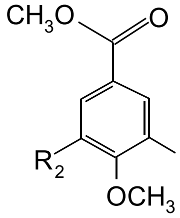


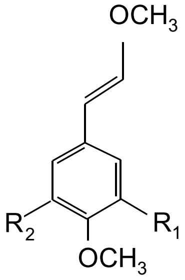
G5 & S5



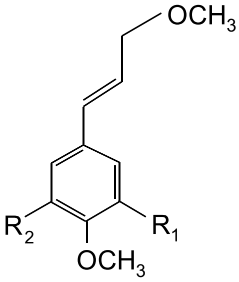
P6, G6 & S6



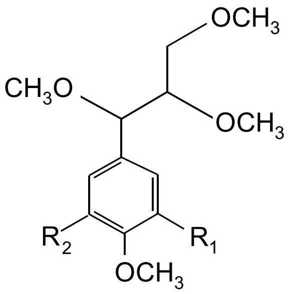
G7, G8 & S8



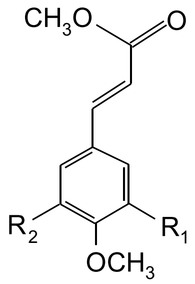
G9 & G13



G14, G15 & S14, S15



P18 & G18



P : R_1=H: R_2=H
G : R_1=OCH_3: R_2=H
S : R_1=OCH_3: R_2=OCH_3

Rawlins et al
Figure 10