# Geochemical Prospection and the Identification of Site Activity Areas

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The archaeological record is much more than distinct, intentionally produced features and objects, such as buildings, earthworks, hearths, ditches, pits, artefacts, and ecofacts. It has long been recognized that human and animal activities on sites and in landscapes result in inputs of organic and inorganic matter, and alterations to the chemical and magnetic characteristics of soils and sediments, in detectable spatial patterns that can survive long-term in the archaeological record. The starting point for the use of geochemistry for site prospection and the identification of past activity areas is the recognition that soils and sediments that have been altered by human and animal activities are also *artefacts*, worthy of being studied with as much attention and advance planning as other archaeological structures, features, and objects. A variety of geoarchaeological techniques can be used to identify the presence, spatial extent, patterning, and sources of these anthropogenic inputs and soil alterations in order to identify the locations of past sites and activity areas. The aim of this Chapter to provide a critical overview of the methods that are currently used, and to provide examples of applications.

The analysis of spatial patterning in the geochemistry of soils and sediments has been deployed at a range of scales, from features, buildings to whole sites and wider landscapes. The most common applications include the identification of the location of settlement sites and graves, the understanding of manuring and other land management practices, the identification of pollution resulting from metalworking, mining and other industrial activities, and the characterization of human and animal activity areas. All such applications seek evidence for elevated concentrations of particular chemical elements relative to the average natural background level *and* the natural variations in that background level in the contemporary soils. It is therefore necessary for all geochemical prospecting studies to include some type of systematic sampling, including the sampling of off-site soils that may be assumed to be unaffected or nearly unaffected by human activity. The challenges of finding suitable comparative control samples, and the identification of an anthropogenic source of chemical elements that are usually present in the natural soil environment to some degree, make geochemical prospecting a challenging endeavour.

An additional challenge is that geochemical prospection and the identification of activity areas can rarely be effective if only a single analytical method is used. Most often, the interpretation of spatial patterning is improved by integrating several methods, which may include pH, electrical conductivity, multi-element or single element (e.g., phosphate) analysis, magnetic susceptibility, organic matter or organic carbon, and lipid biomarkers. Moreover, an understanding of the sedimentological origins and pedological development of the sampled soils is often crucial for the interpretation of geochemical patterning. This understanding can often be facilitated by integrating the results of geochemical prospection with complementary techniques such as geophysics, soil micromorphology, phytolith and particle-size analysis, and the spatial and size distributions of artefacts, ecofacts, and micro-refuse (Jones *et al.* 2010, Milek and Roberts 2013, Shillito 2017, Salisbury 2020). Therefore, geochemical prospecting is often just one link in a longer chain of analytical techniques, and an effective research design requires all of the necessary links to be considered at the planning and sampling stage.

# SOIL SAMPLING METHODS FOR SITE PROSPECTION AND IDENTIFYING ACTIVITY AREAS

Geochemical prospection involves the identification of spatial patterning within features, buildings, sites, and landscapes, and therefore requires a degree of systematic sampling (see also Chapter 48). Random sampling, or judgemental 'spot' sampling, in which specific deposits of interest are targeted, cannot be used because this does not provide the comparative samples necessary to determine what constitutes meaningfully elevated (or depressed) geochemical characteristics and to identify spatial patterning. Instead, soil samples for geochemical prospecting or activity area analysis are usually retrieved using a systematic grid or transect. The size and spacing of the sampling grid typically depend on the scale of the target area. Sampling points on a Cartesian or isometric grid of 10-25 m<sup>2</sup> are common on research projects on the landscape scale, which aim to find new sites, to identify improved/manured fields, animal activity areas, or the extent of burning or metal pollution (e.g., Simpson et al. 2005). For research aiming to identify activity areas on sites or within buildings, it is more typical for a grid of 0.5-1.0 m<sup>2</sup> to be used (e.g., Vyncke et al. 2011, Milek 2012, Carey et al. 2014), but recently higher resolution sampling intervals as small as 0.25 m<sup>2</sup> have been employed in restricted areas such as occupation surfaces and graves (Trant et al. 2021, Sulas et al. 2022). If an area of interest is identified, for example following a preliminary analysis of samples in a field lab, additional sampling points can also be introduced between the initial ones in order to systematically decrease the sampling intervals and increase the resolution of the grid where needed, for example from 10 m<sup>2</sup> to 5 m<sup>2</sup> to 2.5 m<sup>2</sup>. This step-wise, increasingly targeted, sampling design can be especially efficient in remote regions, where there are limits to the numbers or weight of samples that can be transported (e.g., Anderson et al. 2019).

Sample transects, often parallel to each other, perpendicular to a linear feature of interest, or radiating outwards from a central point of interest, have commonly been used in landscapescale studies designed to locate or delineate the boundaries of archaeological sites, potential activity areas, or zones of pollution. For example, Ilves and Darmark (2011) and Mikołajczyk *et al.* (2015) used phosphate analysis of samples collected on transects perpendicular to shorelines to define landing sites and coastal activity zones. Wherever possible, geochemical prospecting uses a sampling grid or transect that is large enough to encompass off-site control samples in order to determine the background levels and amplitude of variation of the local natural soil characteristics (Middleton 2004, Devos *et al.* 2011).

However, even in sparsely populated areas, cultural land use is likely to have had an impact on soils and it is impossible to be confident that apparently 'off-site' samples are truly undisturbed

or uncontaminated (Oonk *et al.* 2009). Where the constraints of the site make it impossible to systematically include off-site samples, such as in sunken buildings, graves, built-up urban areas or intensively used landscapes, judgemental spot sampling of suitable control samples is used out of necessity (e.g., Sulas *et al.* 2022). In principle, it is possible to take suitable control samples many tens of metres away from the study site if the geology, soil type, topography, drainage conditions and land use are all similar (Vyncke *et al.* 2011, Cannell *et al.* 2018). When the object of study is archaeological sediments composed entirely or almost entirely of humanmade or animal-made materials, it has also been possible to identify activity areas without any reference at all to off-site control samples on the basis of clear patterning of clustered high and low values of multiple elements, magnetic susceptibility, organic matter content and electrical conductivity (e.g., Milek and Roberts 2013). Principal components analysis (PCA) has also been used effectively to distinguish between the soil characteristics most influenced by human activities and the soil characteristics most influenced by the underlying geology and soil matrix, making interpretations of geochemical data less dependent on the ability to obtain undisturbed off-site control samples (e.g., Vyncke *et al.* 2011, Cannell *et al.* 2018).

How soil samples are extracted depends on the nature of soils, whether there is surface vegetation, and the sampling depths required (see also Chapter 13). For exposed surface soils (e.g., on a ploughed field) or the exposed sediments on an archaeological site, it is common to simply scrape the surface with a clean trowel or plastic spoon, but soil augers or shallow spadewidth test pits are typically used for collecting samples from subsurface soils (e.g., Anderson *et al.* 2019). Cleaning the sampling tools between sampling points is essential to prevent cross-contamination of soil samples, and when sampling for lipid biomarker analysis it is standard protocol to wear gloves to prevent grease from the skin from entering the sample.

# PHOSPHATE ANALYSIS OF SOILS AND SEDIMENTS

The potential of using geochemical mapping as a prospecting tool in archaeology was first recognized by F. Hughes, working in Egypt in 1911 (Russell 1957:145), and Arrhenius, working in southern Sweden in the 1920s and 1930s, both of whom observed elevated phosphate values associated with archaeological sites (Arrhenius 1931). Following the systematic and seminal methodological work of Cook and Heizer (1965) and Eidt (1977), phosphate (or phosphorus) studies emerged as a key method for locating and defining sites and

investigating specific archaeological contexts (see Bethell and Máté 1989 for a detailed historical review). Due to a number of methodological challenges that complicate the interpretation of phosphate distributions and their sources, which are outlined below, phosphate mapping is rarely used for prospecting in isolation. Instead, soil phosphorus data are usually integrated with artefact distributions gathered by field walking (see Chapter 48), or with other determinations such as magnetic susceptibility (see Chapter 49), soil organic matter content, pH, particle-size analysis, soil micromorphology and phytolith analysis (see Chapter 13) in order to better understand its persistence and spatial distribution. With the decreasing cost and more routine use of multi-element analysis, phosphorus is now often tested as one of a number of archaeologically significant elements determined by multi-element analyses (see below). However, rapid and inexpensive on-site phosphate assays are still valuable, since they can be used during field surveys and archaeological excavations to guide soil sampling and excavation designs, and further soil analysis strategies.

Organic phosphate compounds are present in all living organisms, especially in nucleic acids, phospholipids, the main component of cell membranes, and phytin, the main phosphorus storage reserve in plants. Phosphorus is tightly bound within these organic compounds, but, once it enters the soil, it is gradually released from dead plant and animal residues by bacteria, fungi, and other organisms that secrete phosphatases - enzymes that split separate phosphate ions from organic compounds. Once separated by this process, which is known as 'mineralization', the inorganic phosphate ions  $H_2PO_4^-$  and  $HPO_4^{2-}$  are cycled back into the food chain as plants take up these essential plant nutrients from the soil solution (Iyamuremye and Dick 1996). Inorganic phosphate minerals are also common in rocks and soils. In particular, the apatite group are common accessory minerals in igneous and metamorphic rocks, and, once eroded, can occur in sedimentary rocks and in soils that develop on source rocks. In soils, acids generated by soil microbes and fungi can dissolve and release phosphate ions from apatite, enabling them to be taken up by plants (Gadd 2010). Therefore, even before taking into consideration the effects of human activity, natural concentrations of organic and inorganic phosphorus in topsoils can vary considerably depending on the underlying geology, soil type, surface vegetation, and amount of organic matter present (400-2000 kg/ha). For this reason, it is not the *absolute* value of a phosphate assay but the *elevated* levels of phosphate relative to the natural 'background levels' at a particular site that are used for archaeological prospection or the interpretation of on-site features. Background phosphate levels on any particular site will also have a natural degree of variation due to this range of factors, which is why phosphate

sampling should be done using systematic grids or transects (as discussed above). An individual 'spot sample' could accidentally have tested a very localized and unrepresentative spike in soil phosphorus.

Phosphorus distributions can be used for archaeological prospection because human and animal activities enhance the quantity of soil phosphorus above and beyond natural levels through the addition of materials rich in organic and inorganic phosphorus compounds. The materials linked most often to phosphorus enrichment in soils include animal fodder, dung, food waste, bedding materials, buried human and animal remains, and ashes, in which the process of organic combustion will have already converted organic phosphates to inorganic phosphates (as in Wilson *et al.* 2008, Devos *et al.* 2011). The input of bones and teeth also raise the levels of the inorganic phosphate mineral hydroxyapatite (also called hydroxylapatite), and tooth enamel consists of fluoroapatite, in which some hydroxyl groups have been replaced by fluoride ions.

The use of phosphates for archaeological prospection and site activity area analysis is dependent on its long-term stability and immobility in soils. Only a small proportion of the phosphorus in soils is available to be taken up by plants at any one time, because in soils soluble phosphate ions readily combine with cations in the soil solution to form stable compounds of very low solubility – a process known as phosphorus 'fixation'. These insoluble phosphate compounds are relatively resilient to leaching and can remain in topsoils for long periods of time, enabling their detection in soil surveys long after the date of their initial deposition. However, there are exceptions and caveats to this rule, which have become clearer after decades of research into the dynamics of phosphorus in different soil types under different land-use regimes, and at a variety of archaeological, ethnoarchaeological, and ethnohistoric sites (Crowther 1997).

The ability of a topsoil to 'fix' phosphates and prevent them from moving in solution or being taken up by plants varies according to its pH, texture (particle size), mineral content, and organic matter content. Phosphates are most soluble, susceptible to leaching, and available to plants when the soil pH is neutral, around 6.5-7.2. In more alkaline soils (pH>7.2), phosphate readily combines with calcium cations, forming stable calcium phosphate minerals (e.g., in the apatite group), or adsorbs onto the surface of solid calcium carbonate. In more acidic soils (particularly below pH 5.5), phosphate can combine with iron and aluminium cations to form

insoluble iron phosphate (strengite) and aluminium phosphate (variscite) compounds, or can adsorb onto the surfaces of insoluble iron, aluminium and manganese hydrous oxides. In reducing conditions, phosphate can combine with iron to form crystals of hydrated iron phosphate (vivianite), which is sometimes found in lignite, peat, waterlogged soils and sediments, and archaeological cess pits (Rothe et al. 2014). Phosphates also adsorb to the surface of clay minerals and carbonaceous materials such as charred wood, plant tissues and animal bones, as well as coal and coal ash (Fang et al. 2017, Almanassra et al. 2021). Therefore, clayey soils are better at retaining phosphates for longer periods of time, and where concentrations of clay or charcoal are present on archaeological sites, they can provide additional phosphate reservoirs, which should be taken into consideration when interpreting phosphorus distributions (e.g., Wilson et al. 2008). On the other hand, even soils with high phosphorus sorption capacities can leach phosphates if heavy rainfall or snow melt percolates through it rapidly, for example through larger macropores, due the lack of sufficient contact time between the percolating water and the potential adsorption surfaces (Djodjic et al. 2004). Phosphate leaching has been documented in sandy soils, in reducing soil conditions (e.g., during floods), and, given enough time, it occurs down-profile in podsols (lost from the eluviated horizon and gained in the B horizon below), and downslope in landscapes with hydrologic gradients (Levesque and Hanna 1966, Smeck 1985, Scalenghe et al. 2002). Although all of these factors need to be considered when interpreting phosphate distributions, human and animal activity can add so much phosphorus to soils that the archaeological imprint remains detectible.

The effects of different soil conditions on the forms and persistence of phosphates in soils has implications for the methods used to quantify and interpret it. Moreover, different analytical methods focus on different forms of phosphorus in the soil and the different fractions of phosphorus that can be extracted. These are usually classified in terms of phosphorus chemistry (e.g., organic, inorganic, or total phosphorus), its place in the biogeochemical cycle (e.g., labile, available, adsorbed or occluded phosphorus), or its place in the extraction sequence (e.g., calcium phosphates, recalcitrant phosphates). The variety of classification systems, nomenclature, analytical methods and target phosphate 'pools' (*sensu* Holliday and Gartner 2007:fig. 1) used in archaeological phosphorus analyses makes inter-site assessment and comparisons of soil phosphorus data difficult, even when they are described and referenced in detail. The choices of which phosphate pool to target and which analytical methods or methods to use for a particular project are usually based on an understanding of the soil characteristics

and their likely effects on phosphorus dynamics at the site, the research questions, and the availability of equipment, labour, time, and funding.

Phosphorus analysis involves first the extraction of phosphorus from the soil by breaking the bonds between the phosphorus molecules and their hosts, and then the measurement of the extractant. In archaeological applications, the aim is always to extract either a selected proportion of or all of the anthropogenic phosphorus resulting from past human and animal activities, but it remains a challenge to understand how different extraction methods target specific forms of soil phosphorus and their sources. For this reason, an overwhelming range of techniques have been used. In their comprehensive review of the methods used to quantify soil phosphorus in archaeological case studies, Holliday and Gartner (2007) identified no less than 15 different reagents or combinations of reagents that have been used to chemically digest soil samples for the determination of total or near-total phosphorus. A further 21 different reagents or combinations of reagents were used to extract various fractions of inorganic phosphorus in attempts to quantify different phosphatic compounds. In both cases, ignition of the sample in a muffle furnace (most commonly at 550°C) was sometimes inserted as a step to convert organic phosphate compounds to inorganic phosphate prior to extraction. Organic phosphorus cannot be extracted directly and is instead measured by subtracting the inorganic from the total phosphorus measurements. At least 19 different methods for the extraction of 'available' or extractable phosphorus have been used, each involving different reagents, combinations of reagents, or treatments, which can produce significantly different results (Proudfoot 1976, Holliday and Gartner 2007). Easily extractable phosphorus has also been the focus of portable, simplified, rapid techniques that can be applied in the field (e.g., Schwarz 1967, Eidt 1973, Terry et al. 2000; but see Keeley 1981 for the problems with rapid 'spot tests').

Once extracted, the concentration of phosphate is determined in the laboratory either by colorimetry or by inductively coupled plasma spectrometry (ICP). Replicate sample experiments by Holliday and Gartner (2007) demonstrated that these methods usually produce very similar soil phosphate values. In colorimetry, molybdenum blue is added to the extractant solution to form a phosphomolybdenum blue species, which exhibits different intensities of blue colour proportionate to the orthophosphate and other labile phosphorus species in the extractant (the 'molybdate reactive phosphorus' fraction; Nagul *et al.* 2015). A spectrophotometer is used to measure the wavelengths of light that are either absorbed or transmitted by the sample solution, and the results are calibrated using standards. In ICP, the

extractant solution is sprayed onto an argon gas and super-heated to 10 000 K, forming a plasma of 'excited' ionized atoms, each of which emits a specific light spectrum as it returns to its base state, which is measured by a spectrometer. This technique can use an optical or atomic emission spectrometer (OES or AES) or a mass spectrometer (MS) as a detector, all of which provide very precise measurements of phosphorus and a wide range of other elements at the same time (see multi-element analysis, below). Regardless of the measurement technique used, the phosphorus determination will be dependent on the extraction method.

Several studies have been aimed at evaluating which phosphate extraction methods produce the highest values, which produce similar values, which correlate best with anthropogenic inputs, and which are most efficient and best value for money. These are reviewed by Holliday and Gartner (2007), who also conducted their own experiments using a variety of soil phosphate extraction and measurement methods at three different archaeological sites. They found that strong and concentrated acids, particularly perchloric acid, followed by sulfuric acid and nitric acid, were the most effective at digesting the soil samples and extracting the highest phosphorus values, including the anthropogenic sources of phosphorus. Citric acid and other weak acids extract many forms of phosphate, in some cases as effectively as stronger sulfuricnitric acid and hydrochloric acid extraction methods, but not all anthropogenic phosphates can be determined using this method. Importantly, different extraction methods, when used consistently across the same site, tend to show similar distribution patterns. The implication is that regardless of the extraction method used, phosphate analysis by colorimetry or ICP is a rigorous and useful method for archaeological site prospection and the delineation of site activity areas.

The application of soil phosphorus mapping to archaeology is based on the elevation of the selected form of phosphate above the 'background' levels and variations detected via a systematic sampling strategy. Reviews by Bethell and Máté (1989), Oonk *et al.* (2009) and Devos *et al.* (2011) highlight the range of research questions most frequently addressed through phosphate mapping, including the discovery and delineation of new archaeological sites, the identification of ancient manuring, and the understanding of human and animal activity areas on sites and within structures. Phosphate mapping has also been used to detect ancient shorelines in Fennoscandia, and to model the drop in sea levels adjacent to coastal sites based on the principle that waves bounded and visibly distorted the sites' elevated phosphate levels (Ilves and Darmark 2011, Mikołajczyk *et al.* 2015). Phosphate mapping therefore remains

useful for many archaeological research questions, and direct comparisons of 'traditional' phosphorus analysis with the results of multi-element analysis demonstrate that phosphorus is still the most powerful indicator of anthropogenic additions to ancient soils (Oonk *et al.* 2009, Nielsen and Kristiansen 2014). In addition, portable and rapid field methods that use colorimetry to provide semi-quantitative phosphate assays remain one of the most effective ways to rapidly locate buried sites and soils, and to assess the locations of core activity zones – information that can immediately be factored into the design of excavation and sampling strategies (e.g., Hassan 1981, Lippi 1988, Parnell *et al.* 2001, Anderson *et al.* 2014). Recently, Weihrauch and co-authors have proposed new extraction protocols that may replace the time-intensive process of P fractionation for soil prospecting (Weihrauch *et al.* 2020) and comparisons that seek to overcome the various challenges that heterogeneous environments present in phosphorus prospecting (Weihrauch and Soder 2021).

Nevertheless, due to the difficulties in interpreting elevated phosphate distributions without comparative data to better understand its sources and dynamics, phosphate studies have seen a dramatic drop in the published literature. Even for basic site prospecting, phosphate mapping tends to be integrated with at least artefact and ecofact distributions obtained through field walking or coring. For example, both the levels of elevated soil phosphate and the different densities of artefact scatters were used by Thurston (2002:206-207) to survey a large area in Denmark and to locate Iron Age house plots, village areas between house plots, and the manured fields surrounding the villages. The current state of the art for the use of geochemistry to locate, delimit, and interpret archaeological sites and activity areas is a multi-proxy approach that considers phosphorus distributions alongside the spatial patterning of other elements, pH, electrical conductivity, organic matter, magnetic susceptibility, and, increasingly, lipid biomarkers (e.g., Nielsen and Kristiansen 2014, Markiewicz and Rembisz-Lubiejewska 2016, Anderson *et al.* 2019; see also Chapter 26) (Figures 51.1 and 51.2). The remainder of this Chapter is devoted to a review of these approaches and the ways in which they have been integrated.

<Figs 51.1 and 51.2 near here>

# MULTI-ELEMENT ANALYSIS OF SOILS AND SEDIMENTS

Though phosphorus is by far the most widely measured element in archaeological soils for prospection purposes, many other elements are also affected by human activities and thus can be used as indicators. These include carbon, nitrogen, sodium, and calcium, with more trace levels of potassium, magnesium, sulfur, copper, zinc, and other metals (Holliday and Gartner 2007 and references therein). Whilst measuring these various elements individually might be prohibitively time consuming, the emergence of inductively coupled plasma atomic emission and mass spectrometers (ICP-AES and ICP-MS, respectively) with the capability of simultaneous multi-element detection have simplified such analyses. There are many descriptions available on the principles behind these instrumental methods available elsewhere (e.g., Pollard et al. 2007:chapters 3 and 9, Pollard et al. 2017:chapter 2). Multi-elemental analyses of well-documented historic farm sites showed how elemental concentrations correlate with different activities, aiding in using such information at archaeological sites (Wilson *et al.* 2005). The same authors followed up this study with a review of literature at the time on the subject (Wilson et al. 2008), as have others (Oonk et al. 2009). One of the primary limitations of multi-elemental analysis of soils for archaeological prospecting is the lack of standardization in sampling, processing and measurement (Cuenca García 2015). Bintliff and Degryse (2022) provide a current overview of how such multi-elemental analyses have been used to inform archaeology.

In addition to ICP-AES and ICP-MS, X-ray fluorescence (XRF) can be used to measure elemental compositions of soils either in the laboratory or even *in situ* using portable hand-held XRF instrumentation, usually referred to as pXRF. Caution should be exercised when using pXRF to compare samples, however, as soil moisture and even the thickness of plastic bags in packaged samples can affect elemental measurements (Shugar 2013). Laboratory-based XRF measurements of elements relevant for metalworking showed correlations between those elements and human activities within the Roman town of Calleva Atrebatum in modern day Silchester, Hampshire, UK (Cook *et al.* 2014). Lubos *et al.* (2016) investigated how *in situ* pXRF results compared with those obtained by ICP-AES, finding that some sample preparation methods had little or no correlation with site use or indeed with other measurements of the same soils, though they did find that pXRF is a suitable method for archaeological studies. When used correctly, pXRF is a cost-effective and relatively inexpensive method for doing rapid elemental analyses of soils *in situ* (Save *et al.* 2020).

There are innumerable case studies for the use of multi-elemental analyses in archaeology, and

so we present only a handful here. The determination of activity areas within buildings was one of the early applications of multi-elemental analyses, as discussed by Middleton and Price (1996), first as a pilot study and later followed up with a comprehensive analysis (Middleton 2004). Wells et al. (2000) applied multi-elemental analyses to anthrosols at Piedras Negras in Guatemala, which was later followed up by Parnell et al. (2002a) at the same site, determining statistical correlations between elemental concentrations and activities such as food preparation and craft production. Other sites in Guatemala and El Salvador also showed that elemental analyses of modern and ancient soil geochemistry provided insights on how activities leave chemical traces (Terry et al. 2004), even when sites are abandoned relatively rapidly (Parnell et al. 2002b). More recent work summarized the use of elemental analysis of household floors in sites in Mexico and Italy for determining activity areas as well (Pecci et al. 2017). Multielemental analyses, in combination with geophysical methods, have shed light on past human activities across Scotland in a variety of difficult survey environments (Cuenca-García 2019). Further combining site geochemical analyses with field work and multivariate statistics has shown the importance of context in the interpretation of such measurements, especially at archaeometallurgy sites (Carey and Moles 2017). Danielisová et al. (2017) describe the use of soil geochemistry to investigate the possible function of Viereckschanzen, specific Iron Age sites in Bohemia, finding that they were likely occupied for only short time periods, and may have played complex roles over time.

Though the case studies above show how multi-elemental analyses can be used to determine archaeologically relevant information about past human activities, there remain numerous challenges. Of primary consideration is the careful interpretation of the results, requiring experimental as well as ethno-archaeological research to understand the sources of the observed soil geochemistry. The future of soil geochemistry for site prospection lies in the application of multivariate statistics such as principal components analysis for the analysis of the large datasets.

#### pH ANALYSIS OF SOILS AND SEDIMENTS

Soil pH is a measure of its acidity or alkalinity in an aqueous solution. It was recognized as a tool in archaeological site interpretation by Deetz and Dethlefsen (1963), who used it to characterize midden sediments in profile. But its use in archaeology is usually limited to a

broad chemical characterization of soils or archaeological sediments to assess stratigraphic and taphonomic processes, such as the potential of archaeological deposits to fix or leach phosphates and other elements (see above), and to preserve or deteriorate organic remains, bones and teeth (van Bergen et al. 1998, Canti et al. 2015; see also Chapters 53 and 56). National soil datasets on topsoil pH do not provide enough resolution to characterize the likely preservation conditions on an archaeological site (Reid and Milek 2021), and one or two soil pH tests on an archaeological site are unlikely to be representative of preservation potential across the site (e.g., Salisbury 2013). Localized pH values can be dramatically altered by microtopographic and archaeological features such as depressions, pits and ditches, which tend to hold organic matter and water, and by anthropogenic inputs of acidic organic matter or peat ash, or alkaline wood ash or mortars. Therefore, any systematic use of geochemistry as a prospecting or activity area analysis tool must include the determination of soil pH on the same samples to understand the localized dynamics of different elements. Conducting pH tests on a systematic grid or transect also aids in the interpretation of bone, artefact and charcoal distributions on archaeological sites, organic matter determinations by loss-on-ignition (see below), and the function of soil biota and rates of organic matter decomposition on a site.

pH is a measure of the concentration of  $H^+$  ions (potential hydrogen) on an inverse logarithmic scale, whereby pH values of 1, 2, 3, etc. denote the abundance of  $H^+$  ions at an order of magnitude of 10<sup>-1</sup>, 10<sup>-2</sup> and 10<sup>-3</sup> respectively. Therefore, lower pH values indicate greater numbers of  $H^+$  ions in and greater acidity of the soil solution. Soil pH is determined by measuring the  $H^+$  ions extracted from the soil sample when the dried sample it is mixed with distilled, deionized water at a fixed ratio. The measurement is made with a calibrated electronic pH meter with an electrode that attracts and measures the  $H^+$  load from the soil-water suspension. The method is inexpensive and rapid, and can be easily done in the field, but it is important to use a meter that compensates for the temperature of the solution, which can be especially variable in field conditions.

The relative alkalinity or acidity of a soil is influenced by its parent material, vegetation cover, and organic content, and by anthropogenic inputs, and it in turn plays an important role in the development of different soil types and the preservation potential of soils and archaeological sediments (see Goldberg and Macphail 2006:47 and Campbell *et al.* 2011:5-6 for useful summaries). The 'background' soil pH is most heavily influenced by the soil's parent material. Soils that develop on acid igneous rocks or on sediments derived from strongly weathered rocks

(e.g., siliceous sands rich in quartz and feldspars), are usually acidic (e.g., pH 3.5-5.5), while soils that develop on alkaline calcareous rocks such as limestone or chalk, or on calcareous sands or marls are usually alkaline (pH 7.5-8.5). Since rainwater has a pH of 5.6, well-drained siliceous soils and archaeological deposits exposed to regular rainfall will lose basic cations such as Ca<sup>2+,</sup> Mg<sup>2+</sup>, K<sup>+</sup> and Na<sup>+</sup> as they are replaced by the constant supply of new H<sup>+</sup> ions, and will acidify over time. In addition, the decomposition of organic matter by soil microbes and fungi often lowers soil pH by disassociating and releasing H<sup>+</sup> ions that were associated with organic acids. However, this is dependent on the initial pH of the soil, with increased acidification more evident in acidic soils, and on the nature of the organic matter itself, which affects the availability of anions to be released into the soil (Ritchie and Dolling 1985).

Where systematic pH testing has been conducted alongside the determination of artefact, phosphate, and/or multi-element distributions in site surveys, it has proven to have a localized patterning that is associated with microtopographical features and anthropogenic inputs. For example, Weymouth and Woods (1984) combined pH analyses with phosphate, calcium, magnesium, potassium, iron, zinc, and copper assays and magnetometry to survey French forts in Illinois, USA. They found positive correlations between pH, calcium and phosphate, which were show by subsequent coring to be associated with *in situ* cultural remains such as charcoal, mortar, and limestone floors. Systematic pH and multi-element geochemical prospection at the site of an eighteenth century farmstead and other nearby historical sites in New Jersey, USA, found that anomalous spikes in pH, calcium, phosphorus, potassium, zinc, copper, iron and manganese were consistently associated with anthropogenic activity areas such as houses and kitchens, and were more effective at characterizing site activity areas and targeting areas for excavation than surface and plough-zone artefact distributions (Gall 2012).

At the scale of individual buildings, where closer sampling intervals can be used to provide additional detail about site activity areas, variations in pH have proven essential for site interpretations. In their multi-proxy analysis of occupation deposits in a Viking Age house in Reykjavik, Iceland, Milek and Roberts (2013) found that the wet, organic deposits infilling the metre-wide foundation trench of a post-medieval building had significantly lowered the pH of the tenth century floor sediments a few centimetres below. This in turn had depleted the calcium in the same zone and rendered the bone and burnt bone distributions in that zone unusable. In contrast, elevated pH was positively correlated with elevated calcium, potassium, bone and burnt bone distributions in the former location of a robbed-out oven in a Viking Age pit house

in Iceland (Milek 2012). These case studies illustrate the importance of routine and systematic testing of pH where distributions of artefacts, ecofacts and geochemical determinations are being used for prospection or activity area analysis.

#### ELECTRICAL CONDUCTIVITY ANALYSIS OF SOILS AND SEDIMENTS

Lab- or field-based tests of the electrical conductivity (EC) of soil solutions have so far been used infrequently for geochemical prospecting and activity area analysis. This technique is not to be confused with electrical conductivity geophysical methods, which detect anomalies caused by a combination of soil moisture, texture, compaction, and salinity (Heil and Schmidhalter 2017 and references therein; see also Chapter 49). Soil EC can provide rapid information about elevations or depletions in the salinity or nutrient content of soils and sediments, which may be derived from seawater or seaweed, urine, groundwater (via evapotranspiration), or the soluble phosphates and other nutrients associated with anthropogenic inputs. This makes it a potentially useful field method or preliminary laboratory step, which can guide more expensive and time-consuming sampling and analytical strategies. Moreover, EC determinations on soil extracts can be made at the same time as pH because the sample preparation protocol is identical and there are meters that include dual pH and EC functions.

EC measures how well a solution can carry an electrical current and therefore provides a proxy for ion concentrations. While pH measurements determine the quantity of H<sup>+</sup> ions specifically, EC is a proxy for the total abundance of ions extracted when a dried sample is mixed with distilled deionized water at a fixed soil:water ratio, usually 1:1, 1:2, 1:3 or 1:5. The measurement is made with a calibrated electronic EC meter with two electrodes spaced 1 cm apart. Depending on the concentrations of soluble salts, soil solution EC is typically measured in mS/cm or  $\mu$ S/cm, but  $\mu$ S/cm meters are more precise and versatile because the soil:water ratio can simply be increased if initial measurements exceed the detection limit. EC meters are sometimes integrated with a pH meter, and, like pH, EC is a portable, inexpensive, and rapid method that is easily done in the field.

The EC of soil solutions is related to the presence of polyatomic anions such as orthophosphates  $(PO_4^{3-})$ , nitrates  $(SO_3^{-})$ , and sulfates  $(SO_4^{2-})$ , cations such as  $Ca^{2+}$ ,  $Na^+$ ,  $K^+$ , and  $H^+$ , and anions

such as Cl<sup>-</sup>. Although soluble, available for uptake by plants, and susceptible to leaching from well drained soils, case studies have shown that elevated concentrations of these salts can persist in soils and archaeological sediments in non-random patterns that reflect past human and animal activity. For example, in systematic multi-proxy studies of a Viking pit house and long house on different sites in Iceland, EC distributions were elevated by 10-1000 times in just one discrete floor context in each building, which was limited to specific zones in the eastern side aisles (Milek 2012, Milek and Roberts 2013). While multiple elements, pH, and magnetic susceptibility also showed marked distribution patterns, none mirrored the distribution of EC, implying that this method can provide information not captured by other proxies. In this cultural context, the elevated EC was attributed to salts derived from either urine or seaweed, which could not be detected by ICP-AES.

Due to its portability, soil solution EC can also be employed in the field. Next to the remote Siberian site of  $\widehat{IA}$ rte 6, Anderson *et al.* (2019) sought evidence for early reindeer domestication by sampling multiple buried soil horizons on a 10 m<sup>2</sup> grid over a 3200 m<sup>2</sup> area. They did rapid pH and EC tests in a field lab tent with a Hanna Instruments portable pH/EC meter and then focussed on a zone of elevated EC values in the uppermost buried soil for higher resolution sampling on a 5 m<sup>2</sup> grid for subsequent lab-based phosphate and lipid biomarker analysis (Figures 51.1b and 51.2b). By radiocarbon dating charcoal sieved out of the soil samples in the field lab, they were able to trace the keeping of reindeer at the site from the fifth century CE to present.

# ORGANIC MATTER DISTRIBUTIONS IN SOILS AND SEDIMENTS

Soil organic matter is any biological material originally produced by living organisms that is present in soils or sediments. It is usually at some stage in the decomposition process, ranging from intact tissues of plants and animals to the well-humified, amorphous material known as humus. Most soil organic matter originates from plants, but anthropogenic organic materials deposited in and around archaeological sites have often undergone an additional stage of alteration, including cooking, digestion and excretion by humans and animals. Other anthropogenic sources of organic matter include organic bedding and building materials, waste products of crop production and cooking, waste products of animal skin processing and cloth production, and partially combusted fuel waste. These organic materials and their decomposition products contribute many of the elements and ions determined using the geochemical techniques described above, and for this reason systematic mapping of organic matter content can aid in the interpretation of phosphate, multi-element, pH and EC distributions.

The identification of soil organic matter can be done chemically or by micromorphological analysis of undisturbed, thin-sectioned soil and sediment on petrographic microscopes (see Chapter 13). The advantage of the latter technique is that it shows the original orientation and distribution of organic matter, its current state of decay, and associated biogenic components such as phytoliths, diatoms, faecal spherulites and parasite ova (e.g., Canti and Brochier 2017, Ismail-Meyer 2017, Vrydaghs et al. 2017; see Chapter 38). Micromorphological analysis therefore has great interpretive power, but it is a semi-quantitative technique, even with the use of digital image analysis or point-counting to quantify the visible components, and the systematic mapping required for archaeological prospection and the interpretation of site activity areas requires one or more of the geochemical techniques described in this section (Macphail and Goldberg 2018:93-95). In addition, the origins of organic matter in an advanced state of decay, when cell structure is no longer preserved, cannot be determined optically; this requires organic geochemical techniques such as lipid biomarker analysis (discussed below and in Chapter 26). The state of the art for studying organic matter content of soils is therefore a multi-proxy, multi-staged approach that integrates systematic, quantitative organic matter analysis with micromorphological and lipid biomarker analysis of a smaller, strategic subset of samples.

Many natural factors influence the transformation and movement of organic matter in soils, including climate (temperature, humidity, and the length of the biologically active season), soil texture and drainage conditions, topography, soil pH, the surface vegetation, and the soil organisms present, all of which affect the rate and intensity of biological activity and the potential for organic matter deposited on the surface to physically move into lower soil horizons. In addition to these natural factors, human activities that involve the removal of surface vegetation for fuel, building materials, crops and animal grazing, particular land-use practices such as tillage, irrigation, drainage, and fertilization, and human and animal inputs of organic matter over time (Bot and Benites 2005). The aim of using soil organic matter content as a tool for archaeological prospection and site activity area analysis is usually to locate, quantify, and

identify organic anthropogenic inputs. For this reason, research strategy that includes organic matter mapping must include an assessment of the local soil type, the nature and intensity of biological activity, the history of land use, and the 'background' soil organic matter content and natural variation.

Soil organic matter must be estimated by proxy, and the most common methods for measuring it are loss-on-ignition (LOI) and wet-oxidation (WO). These methods both involve removing the organic matter from a known weight of sieved (<2 mm), oven-dried sample, either by heating (LOI) or by heating combined with chemical destruction (WO), and then measuring the mass lost. WO uses a reagent such as hydrogen peroxide or sodium hypochlorite to oxidize the organic matter, but experiments have shown that there is a risk of incomplete oxidation due to the type of reagent used, the reaction conditions, and the sample size, making it necessary to apply a soil-specific correction factor (Mikutta et al. 2005). LOI is more straight forward since it does not require a reagent, but it does require a muffle furnace that can closely control the oxidation conditions and heating ramp rate, temperature, and duration. There is a wide range of LOI protocols in the literature, which produce different quantifications due to the incomplete combustion of soil organic matter at lower temperatures and shorter ignition times, the removal of structural water from clay minerals, which over-estimates organic matter content, and the destruction of carbonate minerals at temperatures above 600°C, which does the same (Kasozi et al. 2009). A comprehensive methodological review and experimental study by Hoogsteen et al. (2015) concluded that a sample mass of at least 20 g should be used, that ignition temperatures of 500-600°C are needed for complete removal of organic matter (this could be achieved in three hours), and that a clay correction factor based on the clay content of the sample must be used to correct for structural water loss.

More recently, thermogravimetric analysis (TGA) has been developed for organic matter determination. This uses the same principles as LOI and there is no statistically significant difference between their measurements, but TGA uses smaller sample sizes (30-50 mg), is more automated and faster due to the use of shorter ignition times, and records mass loss through the different heating stages in real time, which theoretically could make it possible to distinguish the loss of structural water from clays (Bensharada *et al.* 2022). TG analysers are much more expensive and less readily available than muffle furnaces, and more experimentation is required to assess the measurement variations caused by using such small sample sizes for heterogenous soils and sediments, but due to its potential to eliminate the need

for clay correction factors, and to rapidly speed up the analytical times required for large batches of soil samples, it is likely to grow in popularity.

Considering the importance of organic matter determinations for the interpretation of phosphate and multi-element distributions in soils, it is surprising that LOI, WO and TGA have not been integrated more routinely into geochemical prospection and activity area studies. Crowther (1996, 1997) mapped LOI together with soil phosphate at the Roman fort at Usk, in Wales, and found that LOI aided the interpretation of phosphate variability, both spatially and with soil depth. LOI was also successfully integrated into a series of multi-method geoarchaeological studies of Viking Age house floors in Iceland, playing an important role alongside pH, EC, micro-refuse and artefact distributions, multi-element analysis and soil micromorphology to identify human and animal activity zones associated with inputs of dung, plant materials, and charcoal (Milek 2012, Milek and Roberts 2013, Milek *et al.* 2014).

# MAGNETIC SUSCEPTIBILITY ANALYSIS OF SOILS AND SEDIMENTS

Magnetic susceptibility (MS) is a measure of the ability of a material to become magnetized in the presence of an externally applied magnetizing field. It is used as a geophysical survey technique (see Chapter 49) but perhaps not as widely as other methods, and often only as a preliminary survey technique to guide more focussed techniques (Batt et al. 1995, Dalan 2008). In this mode it is carried out using a portable induction loop in contact with the ground, which generates a local magnetic field, which in turn induces a response from the magnetic materials in the topsoil below – the depth of penetration is dictated by the size of the induction loop, but is typically 30 cm (Johnson 2013). It can also be used in the laboratory, where a number of different types of measurement can be made on samples taken from grids or transects. Iron minerals in the soil are usually responsible for the measured response, but crucially such susceptibility can be enhanced by burning or the presence of decaying organic material, thereby providing survey data which are particularly sensitive to human activity. It therefore offers a cheap and rapid means of survey for the location of areas of past human activity, such as the identification of burnt soils, hearths and hearth residues. It is, however, also sensitive to longterm land use, the evidence for which often survives modern land management techniques (Johnson 2013).

Multiple examples of the use of field-based measurements of MS in archaeological contexts can be found in Johnson (2013). Anderson *et al.* (2019) used field-based measurements of surface soils to locate shallow hearths in Arctic Siberia, as well as laboratory-based MS determinations to locate deeper hearths associated with buried soils exposed in small soil test pits. They found that MS correlated well with distributions of charcoal and ceramics in the same test pits and was an effective means of identifying indigenous camp sites dating to the first millennium CE (see Figures 51.1c and 51.2c).

Examples of the use of laboratory-based MS determinations to aid activity area analysis are provided by Milek (2012) and Milek and Roberts (2013), who analysed the interior floors sediments of tenth century Viking Age houses at the sites of Hofstaðir and Aðalstræti 16 in Reykjavík, Iceland, using pH, electrical conductivity, magnetic susceptibility, loss on ignition, ICP–AES and soil micromorphology, all measured in the laboratory. High MS results were obtained in the vicinity of the central hearth at Aðalstræti 16, and in the location of the robbed-out oven of the pit house at Hofstaðir, but virtually nowhere else. Experiments have shown that temperature, duration, and repetition of burning have a cumulative effect on the MS of soils, indicating that there is potential to use MS to provide important information about the use and longevity of combustion features (Peters *et al.* 2000, Snape and Church 2019).

# BIOMOLECULAR ANALYSES OF SOILS AND SEDIMENTS

Biomolecules, which include nucleotides, proteins, carbohydrates, resins and lipids, have the potential to survive in the archaeological record, and can provide important information on the activities of past humans and their animals, but the degree of survival and quality of preservation is dependent on physicochemical conditions in the depositional environment (e.g., soil pH, redox potential, particle size, temperature, wetness, and biomass) (Evershed 2008, Corr *et al.* 2008, Oonk *et al.* 2012, Cappellini *et al.* 2018). While the analysis of lipids in the organic residues adhering to or in unglazed ceramics is an established technique for identifying the organic materials once stored or processed in them (see reviews in Evershed 2008, Roffet-Salque *et al.* 2017, Rosiak *et al.* 2020; also Chapter 26), the application of organic geochemistry to site prospection and the analysis of activity areas has excellent potential as well, especially when used in conjunction with the other methods described in this Chapter.

Lipids are organic compounds that are soluble only by organic solvents, not by water (e.g., oils, fats, waxes, and resins), making them more resistant to leaching and biodegradation in soil and sedimentary environments than other organic molecules (Evershed 2008, Lloyd *et al.* 2012, Cappellini *et al.* 2018; see also Chapter 26). Lipid analysis is a powerful tool for archaeologists because of the potential of particular compounds, groups of compounds, and compound-specific isotopes to serve as 'biomarkers', providing genus- or even species-level determinations of their plant or animal origins. The combination of their persistence in soils and sediments and their interpretive power lend lipid biomarkers to a range of important applications in archaeological prospection, including the interpretation of land use, vegetation cover, and manuring practices, as well as the identification of activity areas and specific features related to food storage and processing, combustion, toileting, the corralling, housing or burial of animals, and organic flooring or bedding materials. Since lipids can migrate from soil and sedimentary matrices into artefacts, the biomarker analysis of depositional contexts also provides crucial data with which to assess likely environmental contributions to the organic residues detected in ceramics (Heron *et al.* 1991, Whelton *et al.* 2021).

In line with the other prospection techniques discussed in this Chapter, the concentration and distribution of lipids in soils and sediments can only be related to past anthropogenic activity by referencing the 'background' concentrations and proportions of the relevant lipids in offsite control samples. The selection of appropriate control samples can be challenging in many modern environments where there is often a palimpsest of lipid inputs by people, animals, plants and soil fauna, but it forms an important part of the research design. Procedures for the extraction, concentration, analysis, and quantification of lipids from soils and sediments are similar to those outlined in Chapter 26, with variations determined by the target lipids. The quantification of the lipid compounds, fragments, and compound derivatives determined by GC-MS is followed by an analysis of their relative abundance (%) and quantitative comparisons between the proportions of particular lipids in the archaeological soil samples and those in known reference samples. The likelihood of lipid biomarker identification being accurate is therefore dependent on the range and relevance of the reference samples in the comparative database used.

For one class of lipid biomarkers commonly used in site prospection and the identification of site activity areas, faecal steroids (5 $\beta$ -stanols,  $\Delta^5$ -sterols, 5 $\alpha$ -stanols, epi-5 $\beta$ -stanols, stanones, and bile acids), the number of species and diets represented among the faecal reference samples

has been steadily increasing but is still far from comprehensive. Seasonal changes in vegetation availability, livestock pasture ranges, and fodder types have the potential to change proportions of different faecal lipids (Prost et al. 2017, Harrault et al. 2019). For example, seasonal dietary change is marked in domesticated reindeer due to the dominance of lichen grazing in the winter, such that winter and summer diets can be detected in the proportions of different 5 $\beta$ -stanols, and this information has been incorporated into the interpretation of site seasonality (Anderson et al. 2019). The proportions of different 5β-stanols in Neanderthal coprolites found at El Salt, Spain, revealed that Neanderthals mainly consumed meat (indicated by a high proportion of coprostanol), but also had significant plant intake (indicated by the presence of  $5\beta$ stigmastanol: Sistiaga et al. 2014). The expansion and open publication of reference datasets will continue to improve the understanding of how to identify the faeces of wild fauna, how dietary variations affect steroid proportions, and the extent to which soil fauna influence the steroid proportions in archaeological soils and sediments. The quantitative methods used to match the faecal lipids quantified in archaeological soil samples with faecal reference samples are also under constant development, with the analysis of a larger suit of lipids, and the use of either a larger number of lipid ratios or multivariate statistics (e.g., PCA coupled with hierarchical cluster analysis) now enabling more species-specific faeces identifications (Prost et al. 2017, Harrault et al. 2019).

As a geochemical prospection tool, faecal lipid biomarkers have been used for some time to identify agricultural soils amended with animal manure, providing important information about livestock husbandry and the relationship between past agricultural and pastoral systems (Bull *et al.* 1999, 2001, Simpson *et al.* 1999). Species-level identification of faecal biomarkers have enabled them to be applied to the identification of reindeer congregating areas near campsites in Arctic Siberia, pushing back the date of reindeer herding to the mid-first millennium CE (Anderson *et al.* 2019). As a site prospection tool, lipid biomarker analysis is too time consuming and expensive to use on its own, therefore it is usually used in conjunction with (and as a follow-up to) phosphate analysis (Figures 51.1d and 51.2d).

In on-site activity area analysis, lipid biomarkers have a wider range of applications. Hjulström and Isaksson (2009) tested multi-element and lipid biomarker analyses of floor sediments in a reconstructed and seasonally inhabited Iron Age house at the Lejre Exprimental Centre in Denmark and found that faecal lipids effectively identified the cattle byre. Faecal lipid biomarkers also contributed to the identification of human faeces in Pre-Clovis deposits in Paisley Caves, Oregon (Shillito *et al.* 2020), in midden and room fill contexts at Neolithic Çatalhöyük (Shillito *et al.* 2011, Ledger *et al.* 2019), and in a Viking Age building interpreted as a latrine at Hofstaðir, Iceland (Simpson *et al.* 2009). In a multiproxy study of occupation deposits within and outside of an Iron Age roundhouse in Scotland, faecal steroid ratios showed the locations of ruminant dung accumulations (Mackay *et al.* 2020), and the lipid fingerprinting approach helped to identify the presence of horse faeces – assumed to derive from a sacrificed horse – in a furnished Viking Age burial in Denmark where preservation of bone had been poor (Sulas *et al.* 2022). However, in the Viking Age longhouse on the East Mound at Bay of Skaill, Mainland Orkney, faecal stanol ratios indicative of ruminants were present in low concentrations throughout both the human dwelling area and the byre, most likely due to trampling (Doonan and Lucquin 2019).

Building on organic residue analysis of ceramics, previous research demonstrates the possibility of using lipid biomarkers to identify food residues in anthropogenic sediments and structures. For example, in the Bay of Skaill East Mound longhouse,  $C_{18}\omega$ -(o-Alkylphenyl)alkanoic acids, cooking residues only formed by heating  $C_{18}$  polyunsaturated fatty acids (Evershed *et al.* 2008) were found in the hearth and cooking pits (Doonan and Lucquin 2019). Iron Age slab-lined pits in Arctic Norway and cemented sand features on coastal sites in Alaska were rich in isoprenoid fatty acids,  $\omega$ -(*o*-alkylphenyl)alkanoic acids, and bulk  $\delta^{13}$ C values, enabling the features to be associated with the extraction of oil from the blubber of marine animals (Heron *et al.* 2010, Buonasera *et al.* 2015). In a high status Migration Period building at Alby, in Sweden, elevated concentrations of cholesterol in parts of the floor were ascribed to spillage from eating and serving food (Hjulström *et al.* 2008).

Lipid biomarkers are also contributing to the understanding of on-site vegetation (in samples from buried soils) as well as plant materials within anthropogenic sediments. For example, the organic-rich topsoils underlying Neanderthal combustion features at Alcoy, Spain, contained triterpenoids and aliphatic compounds, which are angiosperm biomarkers, but no diterpenoids, which are gymnosperm biomarkers, providing valuable information about the environment of the site (Leierer *et al.* 2019). The suite of vegetation biomarkers (*n*-alkanes, *n*-carboxylic acids, *n*-aldehydes, wax esters and pentacyclic triterpenoids) in a sequence of buried soils associated with a reindeer-herding site in northwest Siberia showed that grasses, sedges and herbs increased while shrubs decreased throughout the period of site occupation, despite a warming climate, most likely due to human and reindeer presence at the site (Harrault *et al.* 2022).

The potential of lipid biomarker analysis to contribute to site prospection and the interpretation of site activity areas is likely to increase further as it becomes better integrated with other geoarchaeological methods, including soil micromorphology. In thin section analysis, decomposed, amorphous organic matter can be described and semi-quantified, but without any diagnostic cell structure the identification of its origins relies on complementary organic biomarker analysis (e.g., Shillito et al. 2011). When suspected organic deposits are encountered on excavations, and are of sufficient thickness for sampling, they can be targeted with bulk samples for LOI, lipid biomarker and phytolith analysis, alongside block sampling for micromorphological analysis (e.g., Shillito et al. 2011, Mallol et al. 2013, Connolly et al. 2019). However, the best method for identifying decomposed organic remains in the thin 'micro-contexts' so often encountered on settlement sites would be to take two undisturbed block samples side-by-side, embedding one with resin for thin sectioning, and using the other for subsampling for lipid and phytolith analyses once the layers of interest have been identified in thin section. An exciting recent development is lipid biomarker analysis of dust drilled from resin-embedded sediment slabs, which enables direct subsampling of the micro-contexts analysed in thin sections manufactured from the same slabs (Rodríguez de Vera et al. 2020). While more research is needed to expand the range of biomarkers that can be characterized with this approach (e.g., to include faecal steroids), and to develop mathematical corrections for the interference of organic resins in the mass spectrometry results, the ability to more closely integrate lipid biomarker analysis with soil micromorphology would represent a stepchange in our ability to interpret activity areas and individual features.

Another potential step-change for geochemical prospection and activity analysis is the improvement to the accuracy of compound-specific radiocarbon date determinations on individual lipid compounds. Developed and validated for  $C_{16:0}$  and  $C_{18:0}$  fatty acids in the organic residues preserved in pottery vessels (Casanova *et al.* 2020) and bog butter (Casanova *et al.* 2021), compound-specific radiocarbon dating analysis (CSRA) also has the potential to be applied to selected lipid biomarkers identified in anthropogenic soils and sediments. Thus, lipid biomarker analysis coupled with CSRA has the potential to provide much-needed absolute dates for archaeological deposits, structures, and field systems lacking preserved bones or plant macrofossils.

# THE FUTURE OF GEOCHEMICAL PROSPECTION AND THE IDENTIFICATION OF ACTIVITY AREAS

Geochemical prospection and the use of geochemistry for the identification and interpretation of on-site activity areas are now at an exciting juncture. The current state of the art is to integrate a range of complementary methods, but the package of methods used, the sampling resolution, the instruments and techniques employed, and the GIS and statistical methods used to analyse the data, are constantly being developed, tested, and validated with ethnoarchaeological, ethnohistoric, and experimental research (e.g., Wilson et al. 2005, Harrault et al. 2019, Trant et al. 2021). This is enabling us to examine the spatial patterning of human and animal activities at an unprecedented level of detail - enabling the 'high definition' archaeology coveted by many archaeologists (e.g., Gowlett 1997, Raja and Sindbæk 2018 and papers therein). Recent methodological advances in many of the analytical techniques discussed in this Chapter have also made it possible to expand the range of applications of geochemical techniques, such as the detailed analysis and interpretation of seemingly empty graves (Sulas et al. 2022). The challenges associated with these important developments are the costs of analysing large datasets with expensive techniques, the high level of expertise needed to do some of the more complex chemical analyses and process the data outputs (e.g., lipid biomarkers and proteomics), and the labour and time needed to process large spatial datasets with multiple techniques. For this reason, the routine integration of relatively simple and inexpensive methods into geochemical prospection (e.g., LOI, pH, EC, magnetic susceptibility), progress towards the use of rapid multi-element techniques such as pXRF, and the adoption of portable instruments that enable analyses to be conducted in the field (e.g., phosphates, pH, EC, magnetic susceptibility and pXRF), are important for this area of archaeological research, and are likely to be increasingly so in the future. Arguably, the ability to conduct increasing numbers of geochemical techniques in the field also has an ethical dimension, because it makes scientific practice more open, understandable, and accessible to other professional archaeologists, community participants, citizen scientists, and the interested public (Shillito 2017, Milek 2018).

As the range of applications of geochemical prospection techniques to new archaeological research questions continues to expand, opportunities are also emerging to apply these techniques to the challenges of modern global sustainable development. For example, detailed spatial distributions of organic matter content, pH values, elements, and the nutrients they

comprise, are as important to precision farmers and landscape and heritage managers as they are to archaeologists. These soil characteristics not only provide information about the history and spatial organisation of human and animal activities, land use, and soil amendment – information essential to archaeologists – but also the potential of these same soils to sustainably support different types of crops and other forms of vegetation today. The zone management approach to precision farming uses information about the spatial variability of soil characteristics to target or reduce the application of macronutrients such as nitrogen, phosphorus, potassium, and magnesium, thereby reducing costs of food production (Heege 2013). Precision farmers, geoarchaeologists, and satellite remote sensing specialists who use light reflectance and the normalized difference vegetation index (NDVI) to map soil characteristics, drainage, vegetation types, and plant health, all collect spatial soil data at a higher resolution than is normally available on existing soil maps (Seelan *et al.* 2003, Pinheiro *et al.* 2017, Webber *et al.* 2019). The collaboration of these different specialists, and open sharing of remote sensing imagery and soil geochemical data, would be mutually beneficial.

Modern farmers, foresters, and other landscape managers have inherited a soilscape altered by the activities of humans and their animals over thousands of years. While soil amendment and drainage by past farmers has often improved the productivity of today's soils, past mining, smelting, artisanal, and industrial activities have left a legacy of toxic heavy metal contamination in soils, and colluvial and fluvial sediments (Knabb *et al.* 2016, Kincey *et al.* 2018, Holdridge *et al.* 2021). Elevated levels of lead, copper, zinc, cadmium, and chromium at past mining, industrial and settlement sites are non-biodegradable, and therefore remain bioavailable to plants, wildlife, domestic animals, and humans, posing an ongoing risk to health (Pyatt 2001, Pyatt *et al.* 2005, Camizuli *et al.* 2018). Geochemical prospection using multi-element analysis therefore has an essential role to play in the identification and evaluation of soil pollution at settlement, mining, and industrial sites, and can provide invaluable data to modern farmers, landowners, and heritage and landscape managers, and can help inform policy on remediation strategies.

Geochemical prospection and the identification of past activity areas have much to offer, not only to archaeological landscape and settlement studies, but also to modern environmental and societal challenges related to the long-term health and sustainable use of soils. The future of geochemical prospection in archaeology is therefore likely to be multi-faceted, with scientific method development, method validation using experimental and ethnoarchaeological studies, and new ancient, historic, and modern applications all having important roles. As we continue to learn more about the intensity and spatial patterning of specific organic and inorganic inputs in soils, and better understand how these are related to past human and animal activities, we hope that both archaeologists and society at large will gain a deeper appreciation for soils and sediments as *artefacts* bear the long-term imprints and legacies of human behaviour.

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# FIGURE CAPTIONS

**Figure 51.1** Soil survey and geochemical prospection at IArte 6, northwest Siberia, showing the results from the uppermost buried A horizons: a) soil thickness, b) field determination of EC, which guided higher resolution sampling, c) magnetic susceptibility with artefacts and ecofacts found in the soil samples, which indicate new camp sites, d) phosphate determination, which guided a more selective sampling strategy for faecal lipid biomarkers. (Data source: Anderson *et al.* (2019) and HUMANOR Project; images by Loïc Harrault; note that the buried horizons identified are not necessarily all of the same date and interpolations are tentative).

**Figure 51.2** Soil survey and geochemical prospection at IArte 6, northwest Siberia, showing the results from the second buried A horizons: a) soil thickness, b) field determination of EC, which continues to correlate with the location of a newly identified camp site and also reveals elevated nutrient levels not associated with phosphate, c) magnetic susceptibility with artefacts and ecofacts found in the soil samples, d) phosphate determination, which guided a more selective sampling strategy for faecal lipid biomarkers. (Data source: Anderson *et al.* (2019) and HUMANOR Project; images by Loïc Harrault; note that the buried horizons identified are not necessarily all of the same date and interpolations are tentative).