CHAPTER 2: ANALYTICAL TECHNIQUES AND METHODOLOGIES

2.1 Introduction

In order to achieve the objectives of this research, several techniques were employed. This chapter summarises these methodologies and briefly describes the instrumentation used. Where appropriate, an assessment of the source of errors and their magnitude is made.

2.2 Geophysical prospection surveys

All the surveys undertaken during this research used standard commercial equipment, described below, and followed the English Heritage Guidelines (David 1995). Surveys by the author were initially carried out over 10m x 10m grids at a resolution of 0.5m, i.e. data were recorded at 0.5m intervals and 0.5m traverses to give a total of 400 data points per grid. Where appropriate, specific anomalies identified from the initial surveys were surveyed in greater detail and further investigations undertaken over 5m x 5m grids at the higher resolution of 0.25m, data being recorded at 0.25m intervals and 0.25m traverses. Where data have been used from other sources (e.g. Vernon 2004), these surveys were undertaken either over 10m x 10m grids (at the same resolution as above) or over 20m x 20m grids at a resolution of 1m, i.e. data were recorded at 1m intervals and 1m traverses.

Grids were laid out using accepted conventional methods, described by Bettess (1992: 6-17) and Clark (1996: 158-164). Additionally, care was taken to construct each grid to an accuracy of ±2cm, compared to ±10cm suggested in David (1995), as it was considered essential that, where surveys were repeated over the same area, continuity of data recording points was maintained for accurate comparisons of survey results.

2.2.1 Magnetometer (fluxgate gradiometer) survey

The general principles of magnetometry are described in depth by Clark (1996: 64ff) and Gaffney and Gater (2003: 36ff, 61ff). Magnetic prospection depends on the existence and state of iron oxides in the ground; the soil material can exhibit a range of weak to strong magnetisations. There are two phenomena which are relevant to the understanding of magnetic anomalies: thermoremanent magnetism (TRM) and the induced magnetism of a material due to its presence in the earth's magnetic field (Gaffney and Gater 2003: 37). There are different mechanisms which cause enhancement to a soil, amongst them burning and fermentation (Le Borgne 1955, 1960) and general anthropogenic activity (Tite and Mullins 1971), and as a result a magnetic contrast exists between a feature and its surrounding soil; this contrast can be the result of TRM, magnetic susceptibility or both, and is measurable by a magnetometer (Gaffney and Gater 2003: 38).

There are several different types of magnetometer instruments (Clark 1996: 66-71) but the one used in this research was the fluxgate gradiometer, described by Clark (1996: 69) and Gaffney and Gater (2003: 61-62). This particular type of instrument was chosen because it is in common use, being readily available and easily operated. The surveys undertaken in this research showed that the fluxgate gradiometer was sensitive enough to record the data from the different types of site encountered and as a consequence the use of other types of magnetometer was considered unnecessary.

Depending on instrument availability, surveys were carried out using either a Geoscan FM36 or FM256 fluxgate gradiometer. Both instruments have a fluxgate sensor separation of 0.5m and an integral data logging capability (the FM256 has a greater capacity for data storage), and were configured for parallel data recording which

ensured a better raw data quality. Although there are minor differences in the mechanics of instrument set up, either could be used without prejudice to the survey process.

The instruments were set up in the recommended manner as described in the Geoscan operating instructions (Geoscan Research 1987, 2003). It was very important to ensure that the fluxgate sensors were aligned and balanced as a poorly set-up instrument will produce results that are degraded by the sensor misalignment and consequently will not accurately record buried features. As the areas being surveyed had the potential to vary in their range of magnetic data (by taking into account the predicted strength of anomalies and background readings), instrument sensitivity was set appropriately for each site to be surveyed. Sensitivity was set to 1nT for iron smelting sites where strong magnetic anomalies are expected to be found; the higher sensitivity of 0.1nT would result in many over-range data points being recorded as the default ("dummy") value of 204.75nT; a setting of 1nT would record "dummy values" of 2047.5nT, which is in excess of the values of magnetic anomalies usually recorded on iron smelting sites (Vernon 2004). A setting of 0.1nT was considered appropriate for lead smelting and charcoal production sites, being the most sensitive for recording the anticipated weak magnetic signals on these sites.

To achieve consistency in the data recording, the surveys were conducted using parallel traverses commencing at the same corner of each grid. The instrument was held as near vertical as possible at approximately the same height above the ground surface on each data collection traverse, and was balanced and zeroed at the start and the zero drift logged on completion of each grid. Although the FM36 and FM256 instruments are both capable of continuous recording, the topographical variations found on the sites surveyed in this research made it difficult to maintain a constant instrument height

during data collection and as result an operator-triggered single-point recording method was used in all the surveys (Vernon 2004). The instrument set up was also prone to drift with time and with changes in ambient temperatures, causing errors which were easily corrected with the regular balancing and zeroing noted above.

2.2.2 Magnetic susceptibility survey

Gaffney and Gater state that magnetic susceptibility is the key in the production of coherent results from magnetic surveys (2003: 38). Not only can the difference in magnetic susceptibility between top soil and subsoils be used to predict the possible outcome of magnetometer surveys, but the spatial variation of susceptibility throughout the topsoil can be an important indicator of archaeological activity (Gaffney and Gater 2003: 38). The general principles of magnetic susceptibility including magnetism of soils are covered in Clark (1996: 99ff), citing the work of Tite and Mullins (1971), Tite (1972), Tite and Linington (1975), Longworth and Tite (1977). Clark also describes the various instruments that may be used in magnetic susceptibility surveys and the survey methods (1996: 101ff). The use of magnetic susceptibility surveys in this research is restricted to a supporting or complementary role to the magnetometer surveys, as advocated by David (1995: 20).

In this research, a Bartington MS2D field sensor with a linked Psion hand-held data logger was employed for area magnetic susceptibility surveys. This instrument was selected as it is the only one commercially and readily available for area survey purposes. Surveys were carried out principally over 5m x 5m grids and occasionally over 10m x 10m grids to support the magnetometer data. The instrument was reset to zero at the end of each line of readings, to reduce drift errors, and data were recorded in a zigzag pattern in each grid. Although the MS2D field sensor offers a fairly rapid

method of data recording, it must be appreciated that the resulting volume specific magnetic susceptibility values are relative and only give an approximation of the laboratory measurable (true) mass specific magnetic susceptibility (David 1995: 21). However, the quantity and resolution of the survey readings were such that reliable interpretations of the data were able to be made, but were often significantly limited by problematic ground surface conditions which led to inconsistent or unreliable readings. This highlighted the main disadvantage of the MS2D instrument: the poor penetration of the signal generated by the field coil. Although the mean diameter of the coil is 18.5cm, the instrument is designed for measuring only the top 10cm of the ground surface and the response at depth drops off rapidly: 50% at 1.5cm and 10% at 6cm (Bartington Instruments 2006). As a result, good coil to ground contact is essential if data measurement is not to be degraded. In addition, readings are also sensitive to the obstructing or diluting effects of deposition and soil movement, and measurements will not be effective if the old surface is overlain by later accumulations of colluvium or alluvium (Clark 1996: 177). In practice, it was always possible to use magnetic susceptibility surveys on the majority of iron smelting sites and charcoal platforms but surveys over some of the iron smelting sites and all the lead smelting sites were not attempted due to very uneven, stony and variable vegetated surfaces.

2.2.3 Earth resistance survey

The principles of earth resistance survey are described extensively by Clark (1996: 27ff) and Gaffney and Gater (2003: 26-34). The methodology including the different instrument electrode configurations or arrays are discussed by Clark (1996: 37ff) and Gaffney and Gater (2003: 56-60). The twin-probe array, which is used in this research and described by Clark (1996: 44-46), is the most commonly used configuration for

earth resistance surveys. It has improved current sensitivity and penetration at shallow depths and has a better resolution than other configurations.

The surveys were undertaken using a Geoscan RM15 earth resistance meter, with integral data logging capability and attached to the frame of a 0.5m twin probe array. This instrument arrangement is in common use, readily available and more practical in operation when compared to multi-probe arrays. Surveys were conducted in a zigzag pattern commencing in the same corner of each grid. Like Vernon (2004), it was quite common to find areas of poor probe contact due to the excessive amount of stone or slag in the ground at some of the sites. The use of the twin-probe frame reduced the risk of recording spurious data; experience by others has shown that multi-probe frames are difficult to use in stony ground as they often need to be moved from side to side to make good contact (Vernon 2004). Clark (1996: 58) states that probe positioning errors do not arise with the twin-probe array: errors due to lateral displacement of the mobile electrodes from the straight line are relatively insignificant.

The main purpose of conducting earth resistance surveys was to determine whether there were any remains of structures associated with the various sites, for example stone slabs or blocks allegedly forming the bases of lead smelting bales. The survey area was limited to that immediately around or near to anomalies identified by the magnetometer or magnetic susceptibility surveys.

2.3 Survey data manipulation and display

Interpretation and presentation of survey data is important in order that the maximum amount of information can be extracted and presented in the most comprehensible and acceptable way. Treatment of survey data is discussed in Clark (1996: 132ff), Gaffney

and Gater (2003: 102-114) and in the English Heritage Guidelines (David 1995: 19). The raw data either recorded by the author or separately collected by others were downloaded into Geoscan *Geoplot* Version 3 software for processing and presentation.

2.3.1 Data processing

Data processing for each of the three survey types followed the guidelines presented in the *Geoplot* Instruction Manual (Geoscan Research 2000), modified where necessary for specific data sets. Where the mean and other values of raw data are quoted in subsequent chapters with respect to geophysical surveys, these values have been derived directly from the *Geoplot* software, not as a separate mathematical exercise. The advice given in the *Geoplot* Instruction Manual has been adhered to regarding the use of the Interpolation function: interpolation (expansion) can increase or decrease the number of data points in a geophysical survey; interpolation (expansion) is a cosmetic device used to give a smoother appearance to the data (without altering the raw data) and can improve the visibility of larger, weak archaeological features (Geoscan Research 2000). The Sin(x)/x expansion method was used initially, followed by the Linear expansion method.

The magnetometer survey data were processed using the "Gradiometer Data Processing" guidelines in the *Geoplot* Instruction Manual (Geoscan Research 2000). The typical processing sequence was to: initially display and review the data, clip the data to reduce the effect of any iron spikes, remove data recording defects such as by edge matching and traverse stripe removal, and finally data enhancement and presentation, which included smoothing and interpolation. Initially, the data were displayed as shade plots and reviewed at ±3 Standard Deviation units (nT) but then changed to Absolute units (nT) for subsequent processing. The majority of data grids

did not require defect removal and enhancement; only a few grids needed edge matching (using the Zero Mean Grid function), spikes removing (using the Despike function) and smoothing (using the Low Pass or Median Filter functions). A series of interpolated plots was produced, showing clipped data ranges in increasing resolution (for example, from ±100nT to ±2nT), from which one or more plots were chosen for reproduction.

The typical sequence for processing magnetic susceptibility survey data was similar to the above with the exception that data recording defect removal was not required. In all the surveys, smoothing of the data was found to be unnecessary. Initial shade plots were reviewed at ±3 Standard Deviation units (10^{-5} [SI]) and subsequently changed to Absolute units (10^{-5} [SI]) for the remainder of the processing sequence. The optimum interpolated clipped data plot for each site was used for reproduction.

For earth resistance data, the typical processing sequence was similar to magnetometer data but with the additional requirement to reduce any geological response. In practice, some of the survey data grids required edge matching and noise spike removal, but none of the grids needed processing to reduce geological response. Initial shade plots were viewed at ±3 Standard Deviation units (ohms) but then changed to Absolute units (ohms) for smoothing and enhancement. A series of interpolated clipped data plots was produced, for example ranging from 100Ω/300Ω to 30Ω/300Ω, from which one or more plots were chosen for reproduction.

2.3.2 Data presentation

The interpolated clipped data plots in each series of plots were individually saved through *Geoplot* as bitmap (.bmp) graphics files and archived. Each bitmap file was

then processed and resaved as a Corel *Draw* (.cdr) file for insertion into documents for publishing; although the *Draw* file sizes were considerably smaller than the original bitmap files, the quality of the data plots was not significantly compromised.

2.4 Sample selection and preparation for laboratory analysis

Samples from iron smelting, lead smelting, glass working and charcoal production were acquired from site or archive sources. However, it was not always possible to obtain samples as some of the sites in this research were Scheduled Ancient Monuments. Those that were obtained were classified for the purposes of selection and preparation as either "solid" or "non-solid". The former were the by-products of the high temperature processes, i.e. slags, residues, crucible fragments and vitrified and semi-vitrified remains of furnace linings, whilst the latter were samples of soil, furnace in-fill and heat-affected clays.

The solid samples were selected from the bulk deposits using morphology as the main criterion and, to a lesser extent, size. The physical capacity of the magnetic susceptibility measuring instruments (detailed in section 2.5) meant that the maximum size of single samples was restricted to no more than 35mm in diameter and 60mm in length. Where a number of the selected samples were physically small, around 1cm^3 each, these were bulked together and regarded as one sample. The amount of iron blast furnace slag, lead smelting slag and glass working residue was limited and consequently the selection of samples was relatively straightforward, if somewhat restricted. In comparison, iron smelting slags were abundant and a specific selection technique developed in a previous study (Powell *et al*. 2002) was used to obtain samples, as it was considered vital to ensure that subsequent sub-sampling remained representative of the type, spread and depth of the original deposits. In this previous study, initial visual

examination of the slag deposits at the Kyloe Cow Beck iron smelting site in Bilsdale, North Yorkshire, had identified three morphological types: Type 1 – a dense tap slag, with small amounts of porosity and with signs of ropey flow on one or more surfaces; Type 2 – a frothy, porous slag, with variable porosity and density; and Type 3 – a magnetic, rust-stained material of varying porosity and density. The relative abundance by weight of each type was estimated to be: Type 1, 70%; Type 2, 25%; and Type 3, 5% (Powell *et al*. 2002). As the iron smelting deposits sampled in this research had similar morphological types and relative abundance, the same technique was used to select the samples for analysis.

The non-solid samples, i.e. soil, furnace in-fill and heat-affected clays, were chosen on location and proximity to the furnace or charcoal platform. The amount of sample taken depended on the bulk quantity available but was usually in the region of 100 to 200g.

Solid samples were washed to remove adhering soil and organic material, and air-dried for several days at a temperature not exceeding 30°C. Non-solid samples were allowed to dry naturally under similar time and temperature conditions, and any organic material removed later when the samples were sub-divided into 50 to 80g amounts in preparation for susceptibility measurements. Only when it was absolutely necessary to do so were sub-samples reduced to a coarse powder, where a minimum of 75% of the sample could pass through a 2mm standard sieve, such as when they contained a higher proportion of stone and/or organic material in comparison with the other sub-samples, or in preparation for XRD analysis (section 2.9) or heating and susceptibility studies (section 2.10). Reduction to a powder could be very time consuming depending on the hardness of the sample.

As a result of the magnetic susceptibility measurements described below in section 2.5, each sample set of slags and residues was shown to have a range of susceptibility values. The three samples within each set which corresponded to the minimum, mean and maximum values of susceptibility in the range measured for that set were selected for microscopic examination. It was not always possible to select these three samples if there were insufficient samples in a set to begin with, in which case the whole set was selected irrespective of susceptibility values. A total of 46 samples were selected and each one prepared for microscopy by the same method (see section 2.8).

2.5 Laboratory analysis of magnetic susceptibility

In the laboratory, the analysis of magnetic susceptibility of samples from a range of different sites was undertaken by measuring the mass specific and mass quadrature specific quantities. This allowed the calculation of the magnetic viscosity of samples, where considered appropriate.

2.5.1 Sample weighing

Samples, prepared as in section 2.4 above, were weighed on a standard bench balance to an accuracy of 0.01g. Wherever possible, the weight of each sample was set in the 50g to 80g range so that the instruments would be within their optimum measuring capabilities; sample weights falling outside this range would lead to greater susceptibility measurement errors. Some of the samples were very small and it was accepted that the susceptibility results would not be as precise as the author would have wished.

2.5.2 Mass specific magnetic susceptibility

Measurements of magnetic susceptibility can be made using a variety of commercially available magnetic susceptibility bridges (see Collinson (1983: 22ff) for a review). For example, Potter *et al*. (2004) used a Molspin susceptibility bridge. In this research, a non-commercial Department-built A.C. Susceptibility Bridge was used to determine mass specific magnetic susceptibility. The instrument consists of a meter which measures the imbalance between two matched coils when a sample is placed in one of them. Since the meter only displays a representation of the total susceptibility (k_T) of the sample, the instrument requires calibration with two standards of known weight and mass specific magnetic susceptibility (χ): manganese sulphate ($\chi = 81.2 \times 10^{-8}$ m^3 kg^{-1}) and high alumina cement ($\chi = 716 \times 10^{-8}$ m^3 kg^{-1}); both standard samples weigh *c*. 50g. The calibration curve of total susceptibility (k_T) *vs*. meter reading so produced is then used to determine k_T of a sample. The mass specific magnetic susceptibility (χ) is calculated from the formula $\chi = k_T / m$.

The bridge was warmed up for about 30 minutes to allow it to stabilise before measurements commenced. In the short term, due to instrument circuitry "noise" the meter reading can change by ±1 digit. Repeated measurements of a sample overcame this error by making an average of the readings. Improved reproducibility was achieved by calibrating the instrument before and after use, and if there were a substantial number of samples to be measured, at intervals during the process. As a result, any changes in the standards' measured values could be observed; it was usual practice to average the two or more standards' readings to reduce the effect of instrument drift. Calibration was seen to remain well within ±1% of its initial value over several hours. It has been demonstrated with a similar instrument to the one used in this research, that there is a 2% spread of magnetic susceptibility values observed for samples weighing

between 20g and 70g, with an optimum weight of 50g (Walker 1980). By ensuring that the samples were in the 50g to 80g weight range noted in section 2.5.1 above, equivalent to a ±1% spread of susceptibility values, the overall instrument error was no more than ±2%.

2.5.3 Mass quadrature magnetic susceptibility

A Pulse Induction Meter (PIM), manufactured by Pulse Technology Ltd. (Abingdon, Oxfordshire) was used to measure mass quadrature specific magnetic susceptibility. The general principles of PIMs are described by Clark (1996: 106) and Gaffney and Gater (2003: 46-47); the instrument used is relatively modern, in that it has one coil to perform the same functions as the two in earlier versions.

The setting-up procedure for the PIM was more complicated than the A.C. Susceptibility Bridge. As the PIM coil may be affected by surrounding metalwork and/or stray magnetic fields, the meter reading has to be reduced to zero using an offset control, thereby minimising the effect of the coil's surroundings. Each time a measurement was taken the instrument was zeroed, to set the amount of offset automatically into the reading. Time constants associated with the measuring process were set to give optimum meter readings: DELAY (delay before measurement made) = 100μs; SAMPLE (duration of measurement) = 50μs; and INTEGRATION TIME (number of measurements made before display) = mid-point of range.

Similar to the A.C. Susceptibility Bridge, the PIM required a calibration curve to be constructed relating the PIM readings to the total quadrature susceptibility (Q). Three standards of known weight and mass quadrature specific magnetic susceptibility (q) were used: high alumina cement (m = 50g, q = 4 x 10^{-8} m^3 kg^{-1}), "BS87" (m = 50g, q =

12.2 x 10^{-8} m^3 kg^{-1}), and "BS87" (m = 38.2g, q = 26.1 x 10^{-8} m^3 kg^{-1}). The Q of a sample was then read off from the resulting calibration curve, and the mass quadrature specific magnetic susceptibility (q) calculated from the formula q = Q / m.

The PIM was allowed to warm up and stabilise for about 30 minutes before measurements were taken. Repeated measurements of a sample overcame meter instability due to "noise" (readings could fluctuate by ±2 digits), by taking the average of several readings. Frequent recalibration of the PIM was carried out to reduce instrument drift; calibration stayed within ±2% of its original value. The overall instrument error was estimated to be no more than ±3%.

2.5.4 Magnetic susceptibility calculations

The weight and meter reading data for the standards and each sample from a set were entered into a Microsoft *Excel* spreadsheet ([sitename]*MSD*) specifically designed to calculate the mass specific and mass quadrature specific magnetic susceptibilities, and magnetic viscosity. The spreadsheet included the production of the calibration curve and created charts which displayed the results as a range of values and, where appropriate, a distribution histogram. Magnetic viscosity (η) was calculated from the formula $\eta = q / \chi$ and expressed as a percentage.

2.6 Archaeomagnetic dating

The principles of archaeomagnetic dating are well documented in the literature; the methodology is based on the principles discussed by Tarling (1983), with subsequent enhancements by Clark *et al*. (1988), Tarling and Dobson (1995) and Batt (1997). Guidelines on producing and interpreting archaeomagnetic dates have recently been issued by English Heritage (Linford 2006).

The geomagnetic field changes both in direction (declination and inclination) and in strength (intensity), and archaeomagnetic dating can be based on either changes in direction or intensity or a combination of the two. Dating by direction requires the exact position of the archaeological material in relation to the present geomagnetic field to be recorded, and so material must be undisturbed and sampled *in situ*. Dating by intensity does not require *in situ* samples but is less precise and experimentally more difficult. This research uses the archaeomagnetic dating by direction method as the instrumentation required is readily available.

If materials and features containing sufficient magnetised particles have been heated to a sufficiently high temperature (>600°C) they may retain a thermoremanent magnetisation (TRM) which reflects the geomagnetic field at the time of last cooling. Suitable archaeological features would include furnaces, hearths, kilns and other fired structures.

In this research, to establish an archaeomagnetic date for a furnace or other heat-affected feature considered to hold TRM, a number of oriented samples were taken *in situ* from the fired material, e.g. from the furnace lining material, heat-affected area or both, using the disc method (Clark *et al*. 1988). Other methods are available but were not considered totally suitable for sampling the type of features found principally on iron smelting sites. Samples were levelled and orientated by means of bubble spirit levels and magnetic compass.

In the laboratory, the samples were trimmed to the maximum dimensions of 2.5cm diameter by 2cm long, so that they would fit the instrumentation. Material left over from sample trimming, hereafter described as remainder material, was retained to allow

further investigations to be undertaken. The remanent magnetism of each sample was measured using a spinner magnetometer (Molyneux 1971), to indicate the relative strength and direction (declination and inclination) of the magnetic field of the sample. The stability of this magnetisation was then investigated by placing selected (pilot) samples in an alternating frequency (a.f.) demagnetiser, where alternating magnetic fields of increasing strength removed the magnetisation step-by-step (Collinson 1983: 308-335). These demagnetisation measurements allowed the identification and eradication of any less-stable or viscous magnetisations acquired after the heating event, leaving the magnetisation of archaeological interest. Other magnetic cleaning methods exist, such as thermal demagnetisation (Collinson 1983: 335-352), but are either not appropriate for the sites in this research or not as readily available as the a.f. demagnetisation method. The pilot samples were selected by these criteria: their declination and inclination values represented the spread of magnetic directions exhibited by all the samples in the set, their initial magnetic intensities were sufficiently high enough to obtain meaningful results, and they were spread physically over the feature under investigation. The magnetic stability of a sample was demonstrated by the construction of a demagnetisation curve (or intensity spectrum) and a Zijderveld plot. The results of the magnetisation directional measurements of a group of samples were represented on an equal-area stereographic plot, which depicted declination as an angle measured clockwise from north and inclination as a distance from the perimeter; alternatively the results were shown on a scatter plot of the angles of declination and inclination for each sample.

The individual magnetic directions (declination and inclination) from the group of samples were entered into a Microsoft *Excel* spreadsheet (*ArchMag*) specifically designed (not by the author) to calculate the mean direction and its precision α_{95}, which

represents a 95% probability that the true direction lies within that cone of confidence around the observed mean direction. The smaller the value of α_{95} the more reliable is the calculation of the mean direction (Tarling 1983: 119). Normally, α_{95} would be expected to be less than 5° for dating purposes; a value larger than this indicates that the magnetic directions of the samples are scattered and therefore do not all record the same magnetic field, whilst a value less than 2.5° typically indicates good precision (Linford 2006). The stability of magnetisation of an individual sample was quantified by entering the magnetic directions (declination and inclination) measured at each stage of the a.f. demagnetisation process into another Microsoft *Excel* spreadsheet (*StabilityCalcs*) specifically designed by the author for the purpose of calculating the Tarling and Symons Stability Index, S_{TS} (Tarling and Symons 1967). For a stable magnetisation S_{TS} would be expected to be greater than 2.5; a value less than this would indicate that the recorded magnetisation was not reliable for dating purposes. Other stability indices exist, such as the Bridon index (S_B) and that of Symons and Stupavsky (S_{SS}), and all stability indices have their limitations (Collinson 1983: 379-386), but S_{TS} is straightforward to use and does give an easily understood representation of a sample's magnetic stability. The stable, mean magnetic direction was corrected to Meriden (52.43°N, 1.62°W), the reference location for the British calibration curve, using the standard method (Noel and Batt 1990). An archaeomagnetic date was then determined by visual comparison of the corrected direction with the British calibration curve in the conventional manner (Clark *et al*. 1988). (Note: new software based on Bayesian statistical methods has been developed which will eventually replace the determination of archaeomagnetic dates through referencing the calibration curve: see Zananiri *et al*. 2007.)

There are several factors which influence the precision of an archaeomagnetic date:

(a) differential recording of the geomagnetic field by different parts of the feature: distortion of the magnetic field in the structure as it cooled caused by magnetic refraction, interaction or anisotropy. Tarling *et al*. (1986), Gentles and Tarling (1988) and Tarling and Dobson (1995) discuss the effects of these phenomena in some detail, the conclusions being that none of them have a major impact on the precision of an archaeomagnetic date;

(b) disturbance of the material after firing: mechanical distortion, e.g. caused by the removal of the bloom from an iron smelting furnace, or movement of a furnace structure subsequent to cooling and over archaeological timescales;

(c) modification of the thermal remanence over time by a viscous element: many archaeomagnetic dating samples have a remanence that comprises at least two components, one acquired at the time of the last cooling of the sample and a viscous magnetic component which has been acquired whilst lying in the geomagnetic field over long time scales (Tarling 1983: 130). The viscous component, usually associated with magnetically "soft" low coercivity material being remagnetised by geomagnetic field variations, is removed through the demagnetisation process described above;

(d) uncertainties in sampling and laboratory measurements: according to Clark *et al.* (1988), levelling of samples can be achieved to within ±0.125° and azimuth to ±0.25°, although in practice these values are more likely to be ±0.5° (C.M. Batt pers. comm.). The high sensitivity of modern spinner magnetometers means that they are capable of measuring the direction and intensity of remanence of a single specimen to within 1° and 2% respectively (Clark *et al.* 1988). Although measured with this high degree of precision, the spread of uncertainty, represented by α_{95}, can be minimised by the collection of several samples from the same source material,

between 15 and 20 where site conditions allow. Errors in orientation and measurement should be averaged out when 5 or more separately oriented samples have been obtained from the same site, such that the overall orientation and measurement error on the mean direction should be around 1 to 2° (Tarling and Dobson 1995; citing Tarling 1983).

(e) error margins in the calibration curve and uncertainties in the comparison of the magnetic direction with the calibration curve: the British calibration curve is compiled from direct measurements of the geomagnetic field, which extend back to AD1576 in Britain, and from archaeomagnetic measurements from features dated by other methods, these having their own spread of uncertainties. Because the geomagnetic field changes spatially, data for the calibration curve can only be drawn from within an area around 1000km in width and all magnetic directions must be corrected mathematically to a central location (Noel and Batt 1990). Currently British archaeomagnetic dates are calibrated by visual comparison to the calibration curve published by Clark *et al*. (1988), but this method takes no account of the errors in the calibration curve itself and an alternative method may also be used (Batt 1997), although it gives a larger error margin on the date but is a better reflection of the actual error.

(f) spatial variations of the geomagnetic field: as well as the large-scale variation alluded to in (e) above, the geomagnetic field over an archaeological site cannot be assumed to be uniform since both natural and artificial features can have sufficient magnetisation to cause small, localised distortion (Tarling and Dobson 1995). Natural features include large scale geological magnetic anomalies, whilst examples of artificial features are iron or steel fencing and pipework, and archaeological features which have magnetic characteristics such as kilns or furnaces. The magnetisation associated with complex electromagnetic events, i.e.

lightning, does not produce a uniform magnetisation and can result in a very high remanent magnetic intensity and randomised directions compared to the natural remanence (Maki 2005); lightning is not, however, considered to cause significant errors (Tarling and Dobson 1995; citing Tarling 1983).

Given the number of different factors, in practice, it is not possible to put forward a general figure for the precision of archaeomagnetic dates; with the present British calibration data, the practical limit on the maximum resolution of dates is around 50 years at the 95% confidence level (Linford 2006: Table 1.2).

2.6.1 Spinner magnetometer

The instrument used for determining the remanent magnetism of an archaeomagnetic dating sample was a Molspin large sample spinner fluxgate magnetometer. It is a highly sensitive, laboratory-based, slow speed instrument, connected to a computer running a Microsoft *Windows*-based software program (*Spinner*) for the computation and display of declination, inclination and intensity of magnetisation (measured in mA m^{-1}). The principles of operation are given in Molyneux (1971) and the Operator's Manual (Molyneux Ltd. n.d. (a)).

Samples were spun at 6Hz about a vertical axis inside a ring-shaped fluxgate surrounded by a triple layer cylindrical MuMetal shield; the output signal was integrated over 6 seconds (short spin) or 24 seconds (long spin) and then displayed as two orthogonal horizontal components of magnetisation. The instrument was calibrated using a standard of known magnetic intensity and the controls were set at maximum signal gain and an initial attenuation of "x 1". A small number of the samples had large magnetic intensities which required the signal attenuation setting to be altered to "x 10";

none of the samples had very small intensities requiring the use of the long spin period. To obtain complete directional results for each sample, a sequence of four measurements was performed with the sample in different orientations. Whilst the *Spinner* program has the capability of accepting a maximum of six different sample orientations, the last two measurements are not required for the standard-sized samples for archaeomagnetic dating. The output signal produced for each sample position was fed to the *Spinner* program. At the end of the sequence, the program calculated and displayed the directional and intensity results. The process was repeated for all of the samples to be measured and the complete set of results entered into the *ArchMag* spreadsheet noted above.

Provided the magnetic intensity of a sample is greater than the noise level and sensitivity of the instrument, then a spinner magnetometer will be capable of measuring the direction and intensity of a sample's magnetisation to within ±1° and 2% respectively (Clark *et al*. 1988; Linford 2006). Allowing for the need to make several measurements on a sample, such as during the stepped demagnetisation process (see section 2.6.2 below), it should still be possible to achieve measured directions and intensities to within 2 to 3° and 5% respectively (Linford 2006).

2.6.2 Alternating frequency (a.f.) demagnetiser

A.f. demagnetisation was carried out using a Molspin shielded demagnetiser (Molyneux Ltd. n.d. (b)). Each pilot sample was subjected to stepped a.f. demagnetisation in fields of 2.5, 5, 7.5, 10, 15, 20, 30, 40, 60, 80 and 100mT (peak applied field), with the remanence being measured by the spinner magnetometer after each step. Other researchers use fields of 12.5 and 50 mT in addition to the above, but the author

considers these extra steps as unnecessary as they do not add any further significant information.

The trimmed sample was put into a plastic holder and the holder placed onto the instrument's rotation platform; starting the rotation has the effect of a tumbling motion on the sample. The rotating sample was inserted into the coil of the demagnetiser and the demagnetisation process initiated. The field in the coil, alternating at around 180Hz, rises at a fixed rate to the set value and when this is reached the field is held for about 5 seconds before being reduced to zero at a rate set by the operator; normally the slowest rate of decrease is used, i.e. 4μT per Hz. When the field reached zero, the rotating sample was withdrawn from the coil, rotation stopped and the sample removed to the spinner magnetometer for directional and intensity measurements.

2.7 Morphological examination of samples

A visual examination of each sample, selected from the bulk deposits and subsequently measured for magnetic susceptibility, was carried out before thick sections were cut and an assessment made of the density, porosity and general coloration. An estimate was made of the size of vesicles and any unusual features such as surface flow marks, attached stone or embedded high iron content material causing localised discoloration noted.

2.8 Microscopy

Two methods of microscopic investigation were employed: optical and scanning electron. Firstly, each sample was studied internally by optical microscopy, and in greater detail than the morphological examination, for evidence of iron content and

secondly, examined using a scanning electron microscope which allowed the elemental analysis of the sample material.

In preparation for microscopic examination, thick sections of each sample were cut using a diamond wafering blade attached to a slow speed saw, mounted in cold-setting compound, ground and polished to a 1μm finish.

2.8.1 Optical microscopy

Examination under reflected light of the mounted thick sections allowed further assessment of sample porosity, and the observation and determination of different mineral and free-metal phases (usually distinguished by varying shades of grey). Examples of these phases are, in the case of iron smelting slags, laths of fayalitic material, dendrites of iron oxide (wüstite) and prills of metallic iron.

The instrument used was a Nikon *Optiphot* reflected light binocular microscope, with a 25x, 50x, 100x, 200x and 400x multi-lens arrangement. Images were taken of areas typical of each mounted sample, using an e-REC *EPS-145CF* camera attached to the microscope and linked to Unibrain *Fire-i* image capture software. Images were scaled either 50μm, 100μm or 200μm depending on sample and area of interest.

2.8.2 Scanning electron microscopy

After carbon coating, the mounted samples were further examined using an FEI *Quanta 400* scanning electron microscope (SEM) operating in high vacuum mode and quantative analyses obtained with an attached INCAx-sight energy dispersive X-ray (EDX) analyser and backscatter electron detector. The SEM was set up with the following configuration: operating voltage = 20kV, filament current = 2.0 to 2.1A,

emission current = 98 to 105μA; operating pressure = 1.0 to 1.5 x 10^{-5} Torr; spot size = *c*.6 consistent with achieving a maximum detector dead time of 50% and an acquisition rate of up to 4.5k counts per second. The SEM was calibrated with a cobalt standard. The image of each sample was scanned for features which could be described as typical of the sample material; two of these features, designated as sites of interest, were selected and within each site two areas and two or more spots were chosen for examination. Analysis of the resulting spectra was carried out using INCA *Microanalysis Suite* software (Oxford Instruments Analytical Ltd).

2.9 X-ray diffraction analysis

Specifically selected non-solid samples were prepared for XRD analysis by being reduced to a coarse powder as described in section 2.4 above. Sample analysis was undertaken using a Bruker *AXS D8 Advance* XRD instrument, operating at 40kV and 40mA, locked coupled in continuous mode. The wavelengths of the X-rays emitted from the copper (Cu) source were: $K_{\alpha 1}$ = 1.5406 x 10^{-10} m and $K_{\alpha 2}$ = 1.54439 x 10^{-10} m; the K_{β} emission was filtered out using a crystal monochromator. XRD measurements of each sample were taken over a 2θ range of 5° to 140° in steps of 0.015°. Analysis of the results was attempted using ICDD *PDF-4 Full File 2004* relational database software. For a full treatment of XRD theory and practice, the reader is referred to any or all of Clegg *et al.* (2001), Cullity (1978), Dyson (2004), Hammond (1997) and Weller (1994).

2.10 Heating and susceptibility relationship studies

Experiments were conducted to ascertain the effect of heating on the susceptibility of selected samples. Two similar methods were employed, the first being analysis by fractional conversion and the second, a variation where samples were simply heated under oxidising conditions.

2.10.1 Fractional conversion analysis

Magnetic susceptibility is widely used in archaeological prospection but one major disadvantage is that it is substantially influenced by natural factors, i.e. soil parent material and underlying geology, which affects the overall concentration of the soil and the quantities of magnetic minerals present (Crowther and Barker 1995; Crowther 2003). Areas of enhancement, therefore, may arise from human activity and/or natural factors (Tite 1972). Fractional conversion is a methodology which is used to differentiate between anthropological enhancement and naturally-derived magnetic susceptibility, through a process of heating under controlled conditions. A sample's original mass specific magnetic susceptibility (χ) and its maximum potential magnetic susceptibility (χ_{max}) are determined, from which the fractional conversion, the ratio of χ to χ_{max} (expressed as a percentage), is calculated; it is a measure of the extent to which the potential susceptibility has been achieved in the original soil and is used as an indicator of the presence and strength of the human effect, although it is only reliable over uniform geology (Tite 1972; Scollar *et al*. 1990; Crowther and Barker 1995; Clark 1996: 180; Crowther 2003).

The method broadly followed that of Tite and Mullins (1971), Tite and Linington (1986), Crowther and Barker (1995), Clark (1996: 180), and Crowther (2003), but with some variations (Dewar 2000). The process involved heating a sample to a high temperature in reducing conditions and then reheating it to the same high temperature in oxidising conditions which enhanced the sample to its maximum potential magnetic susceptibility. Selected soil or clay samples were first reduced to a powder (section 2.4). The initial (original) mass specific magnetic susceptibility (χ) was measured using an A.C. Susceptibility Bridge (section 2.5.2). Approximately 20g of sample material mixed with 2g of ordinary (plain) flour was placed in a graphite crucible and covered with a

5cm layer of charcoal powder; flour was used to ensure that there was sufficient organic content in each sample and the charcoal provided a seal to facilitate the required reducing conditions. Baumann (2004) reported that there is no discernable difference between using charcoal or graphite powder, the latter used by Dewar (2000). The crucibles were placed in a Carbolite furnace where they were heated to 650°C, soaked at this temperature for one hour (to ensure that the samples were fully reduced) and allowed to cool to room temperature. When cooled, the samples were removed from the graphite crucibles and separated from the charcoal. After reweighing, the mass specific magnetic susceptibility was measured to ascertain the intermediate enhancement of each sample. The samples were then placed in open porcelain crucibles, returned to the furnace and reheated to 650°C under fully oxidising conditions. After soaking for one hour at this temperature followed by cooling, the samples were reweighed and the mass specific magnetic susceptibility remeasured to determine the final enhancement (χ_{max}).

A total of 8 samples were chosen for fractional conversion analysis: all were natural clay samples from four iron smelting sites and an experimental charcoal production site (see Chapter 6). All the data were entered into a Microsoft *Excel* spreadsheet (*FractionalConversionMSD*) for calculation of each sample's fractional conversion.

2.10.2 Sample heating under oxidising conditions

Samples of natural clays from the same sites as in section 2.10.1 above were specifically selected in order to determine the relationship between heat-affected clays and their susceptibilities (as one possible means of estimating the operating temperature of an iron smelting furnace or similar structure). Approximately 20g of each sample were placed in open porcelain crucibles and heated in a Carbolite furnace for one hour, through a range of temperature steps from 50°C to 750°C. At each step, after cooling

the mass specific magnetic susceptibility of each sample was measured using an A.C. Susceptibility Bridge. Data were entered into a Microsoft *Excel* spreadsheet (*NatClayTemperatureMSD*) for susceptibility/temperature analysis.