Fine particle magnetic mineralogy of archaeological ceramics

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Abstract. This study investigated the magnetic mineralogy of a worldwide collection of archaeological pottery. The mineral types, the mass fractions and the domain states of the constituent magnetic fine particles were elucidated from a range of measurements including magnetic hysteresis behaviour, the acquisition of isothermal remanence, low field susceptibility and thermomagnetic curves. The magnetic mineralogy of most samples was dominated by magnetite. Titanomagnetites with limited titanium substitution and cation deficient magnetites (indicative of low temperature oxidation) were dominant in some samples. Haematite was detected in 53% of the samples, but seldom contributed much to the saturation magnetization. Magnetic particle sizes are skewed to smaller sizes, with sherds mostly having a large superparamagnetic or a stable single domain fraction. Low temperature susceptibility data suggest that 30% of samples had some multidomain component. The percentage by mass of magnetic material in the ancient pottery studied was less than 0.8% for all but one of the samples and the majority of samples contain less than 0.3% by weight of magnetic fine particles. The presence of low temperature oxidation in many samples and the occurrence of a multidomain component in a third of the collection suggest that ancient pottery may not always be suitable for determining the intensity of the ancient geomagnetic field.

From the beginning of the Neolithic (literally the “new stone age”) onwards pottery fragments (potsherds) become common and metallic objects appear regularly from the Early Bronze Age. The magnetic properties of many such materials have been investigated for both archaeological and geophysical purposes. The accurate radiometric dating of many artefacts, such as kilns and ceramics, has enabled magnetic information derived from such objects to be used to establish curves which define the temporal variation of the Earth’s magnetic field in several geographical regions [1, 2]. The archaeological information that can be obtained from magnetic measurements includes dating (from variations of the direction and intensity of the Earth’s magnetic field), manufacturing technology and determining the provenance of artefacts [3, 4].

Here, the magnetic properties of a collection of ancient ceramics were investigated to determine the mineral types, the mass fractions and the domain states of the constituent magnetic fine particles. The sample set comprised a broad range of pottery sherds from various locations including the U.K., mainland Europe, China, Peru and North America (figure 1). The samples ranged widely in age from 3400 BC up to 1910 AD, for details see reference [5].

Thermomagnetic curves and particularly the Curie temperatures were used to identify the magnetic mineralogy present. High field thermomagnetic behaviour was measured in air using a horizontal Curie balance. Samples were cut from the artefact and the outer section removed to reduce the effects of surface weathering. In the simple case of a sample with a single magnetic mineral type, the
resulting thermomagnetic curve shows a well-defined transition from an ordered magnetic state (convex curve) to a disordered paramagnetic state at the Curie temperature. Curie point temperatures were determined from the intersection of the tangents to the steepest part of the curve and to the paramagnetic curve. Room temperature magnetic hysteresis loops were obtained from crushed samples (to eliminate any intrinsic gross alignment of the magnetic particles) using a vibrating sample magnetometer with a magnetic field up to 1 T. The magnetic hysteresis data were adjusted to remove the contribution of paramagnetic minerals when determining magnetic parameters. Stepwise isothermal remanence acquisition (IRM) with magnetic fields up to 4 T was carried out at room temperature using pulse magnetization. The remanent magnetization was measured with a spinner magnetometer. The resulting curves were analysed using IRMFIT [6]. Measurements of magnetic susceptibility at low fields were used primarily to investigate the domain states of magnetic minerals. The susceptibility was measured at two frequencies, 0.47 and 4.7 kHz at room temperature. The variation of susceptibility from -196 °C up to room temperature was also measured.

The thermomagnetic behaviour was summarized by assigning samples to several categories based on their Curie point temperature and the thermomagnetic behaviour. Category (I) samples have Curie points between 565 °C and 590 °C, within 10-15 ° of the Curie point of pure magnetite (figure 2a). Category (II) samples have Curie points above 585 °C and are considered to represent low temperature oxidized magnetite (figure 2b). Category (III) contains samples which have mean Curie temperatures less than 565 °C, attributable to magnetites with limited titanium substitution (figure 2c). Category (IV) samples show thermomagnetic behaviour consistent with the presence of titanomagnetites which have been oxidized to some extent at low temperature. Category (V) samples contain two Curie temperatures which are clear on both heating and cooling (figure 2d). These samples contain a near magnetite phase and a high titanium content phase. For the remainder of samples the ferrimagnetic mineralogy could not be determined from the thermomagnetic behaviour.

The most commonly occurring Curie points are between 570 °C and 590 °C, indicating the presence of magnetite (figure 3a). For lower Curie temperatures the degree of titanium substitution was calculated [7] and the maximum content observed in this collection was x=0.13 for Tc = 475°C, where x is the amount of titanium substitution in Fe_{3-x}Ti_xO_4. The distribution of Curie points above 570-590 °C may be explained by the presence of partial low temperature oxidation of magnetite.

The heating and cooling curves obtained in the thermomagnetic study also reveal chemical and structural changes that can occur as a result of thermal treatment. Approximately 17% of the samples show near-reversible thermomagnetic behaviour (e.g. figure 2c), consistent with thermally stable
magnetite. Some samples show an increased magnetization of up to 27% on cooling (e.g. figure 2a). This could be due to oxidation of titanomagnetite into magnetite and ilmenite. Reduction of magnetization on heating can indicate the presence of cation deficient magnetite producing an intergrowth of haematite and magnetite on inversion (often an inflexion in the heating curve around 250-380 °C e.g. figure 2b). The occurrence of low temperature oxidation and the behaviour of partially oxidised magnetic minerals when heated is complex and reported behaviour is varied [e.g. 8, 9]. For a detailed discussion see reference [5].

IRM data show a range of remanent coercivity distributions (see figure 3b). The low coercivity distributions are attributed to magnetite or titanomagnetite, in agreement with the thermomagnetic analysis. The high coercivity fraction indicates the presence of haematite. Haematite was present in 53% of the samples, but usually contributes less than 10% to the saturation isothermal remanence (see figure 3c). The magnetic hysteresis loops from most of the sherds indicated a single mineral species saturating below 600 mT along with a significant paramagnetic component (figure 4a, 4b). Although IRM acquisition analysis indicates at least 50% of the sherds contained haematite, the IRM measurements show that the coercivity of haematite minerals is often greater than 1 T so the contribution of haematite in fields of less than 1 T would be typically very small and swamped by the stable ferrimagnetic, paramagnetic and superparamagnetic components in hysteresis loops. Samples with a large haematite fraction produced hysteresis loops that did not saturate in 1 T. Within these samples the hysteresis loops changed from open loops to constricted loops (figure 4c), as the haematite fraction increased.

The mass fraction of magnetic material in a sample was estimated by dividing the measured saturation magnetization (after removing the paramagnetic contribution) by the value of mass.

Figure 2. Examples of the thermomagnetic behaviour of ancient pottery sherds. See text for details.
Figure 3. Magnetic mineralogy data for the sample set, (a) the distribution of Curie temperatures, (b) the distribution of the maximum IRM remanent coercivities for the low and high field components and (c) the percentage contribution of haematite to the saturated isothermal remanence.

magnetization, $M_s$ for magnetite, 92 Am$^2$kg$^{-1}$ (a reasonable approximation for most of the samples). The mass fractions were below 0.8 % for all but one of the samples and the majority of samples contained less than 0.3 % by weight (figure 5a). The saturation remanence ratio $M_{rs}/M_s$ can be used to provide some information about domain state [10]. Figure 5b shows the distribution of $M_{rs}/M_s$ ratios has a broad peak between 0.16 and 0.38, suggesting either a predominantly pseudo-single domain particle size distribution or a distribution containing single domain particles combined with either, or both, superparamagnetic and multidomain particles.

Information about the domain states of the ferromagnetic particles was also obtained from susceptibility measurements by first subtracting the paramagnetic susceptibility (obtained from magnetic hysteresis measurements) and then removing the effect of the mineral concentration by dividing the ferromagnetic susceptibility by the saturation magnetization. This value is termed the ‘reduced ferromagnetic susceptibility’ [11], and depends only upon the domain states and composition of the ferromagnetic particles. The maximum value of the reduced ferromagnetic susceptibility for remanence carrying magnetite particles is $7.6 \times 10^{-6}$ mA$^{-1}$ (calculated from data in reference [12]). Figure 5c shows that most of the samples have higher reduced ferromagnetic susceptibilities, indicating a significant superparamagnetic contribution. Low temperature susceptibility measurements confirm the presence of superparamagnetic particles, with 82% of the samples being dominated by superparamagnetic behaviour or indicating a large superparamagnetic component combined with a (small) multidomain component (about 30% of the samples showed a susceptibility peak between -145 ºC and -155 ºC indicative of multidomain susceptibility behaviour). Combining the data with magnetic hysteresis measurements shows that the superparamagnetic particles can account for between 5 and 85% of the ferromagnetic particle content with the distribution peaking between 30-50%.

Figure 4. Some examples of magnetic hysteresis loops obtained from ancient ceramic samples.
Figure 5 Magnetic mineralogy data for the sample set, (a) the mass fractions of ferrimagnetic particles, (b) the distribution of remanence ratios and estimates of equivalent stable single domain content and (c) the distribution of reduced ferrimagnetic susceptibility.

The magnetic mineralogy of ancient ceramics is often suited to archaeointensity determinations (the magnitude of the ancient geomagnetic field) because of the high fraction of stable single domain particles. However, the presence of some multidomain particles in about 30% of the samples suggests problems may result from the more complex behaviour of these particles [13]. Significantly, archaeointensity determinations may also be affected adversely by the presence of low-temperature oxidation (via a chemico-viscous remanence [14]). Caution is also needed as the particle size distribution often straddles the superparamagnetic-stable single domain boundary implying a sensitivity to the acquisition of viscous remanence.

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