Magnetic properties of fired clay (bricks) possibly containing epsilon iron (III) oxide

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Abstract. We investigated bricks with ages from modern to late 19th century. The experimental and theoretical analysis of hysteresis loops and magnetization (ARM, IRM) acquisition curves show presence of two magnetic phases with high and low coercivity, respectively, which might be related to nanoparticles of oxidized and/or cation-substituted magnetite and epsilon iron (III) oxide. The fired clay (bricks) thus can be viewed as a model system in which epsilon iron (III) oxide forms readily.

1. Introduction

Magnetic nanoparticles are promising materials in many fields of science and technology. Among these, the rare polymorph of iron oxide (III) — ε-Fe₂O₃ is attracts growing interest because of its high coercive force and spontaneous magnetization, making it a potential material for a stable non-volatile digital memory with high recording density [1]. Besides, ε-Fe₂O₃ is a multiferroic at room temperature, which can also increase the recording density of information [2]. Polymorphs of iron oxide (III) can also serve as highly active photocatalysts in sunlight-driven hydrogen production from aqueous solutions containing oxygen bearing organic compounds [3]. In geophysical context, ε-Fe₂O₃ has been recently found to be widespread in archaeological ceramics, the major recorder of the Earth’s magnetic field for the last 10,000 years [4,5].

In this work, we study the properties of magnetic nanoparticles of iron oxides in fired clay products (bricks) produced in late 19th to 21st centuries. Brick samples were studied by vibration sample magnetometry, SQUID magnetometry, electron microscopy and X-ray diffractometry. An analysis of experimental data was carried out similarly to [6,7]. Theoretical modeling of the magnetic states of heterophase particles of iron oxides was also carried out.

2. Materials and methods

2.1. Materials

The studied samples come from two sources:

- The Modern collection (3 samples) consists of modern bricks locally produced in Leningrad region.
- The Valaam collection (7 samples) includes samples taken on the islands of northern Ladoga Lake from the ruined church buildings. These bricks, as a rule, bear the sigils of production facilities allowing to date the bricks by late 19th – early 20th century and to pinpoint the production area as east-central Karelia.

The internal structure of modern bricks appears heterogeneous. A less strongly fired area which has a characteristic black color is seen in the center of the brick. This was taken into account when studying the samples. Bricks from the Valaam collection do not have this feature.

2.2. Experimental methods and theoretical modeling
The morphological structure and elemental composition of the samples were obtained using a Hitachi S-3400 N scanning electron microscope (SEM) equipped with a wavelength dispersive spectrometer WDS-INCA 500.

Phase composition of the samples was studied by X-ray diffraction (XRD) using a D2 Phaser diffractometer (Bruker, Germany). The software package for radiograph analysis PDXL-2 (Rigaku, Japan) and X-ray diffractogram database PDF-2 (International Center for Diffraction Data, 2011) were used to analyze the spectra.

Hysteresis loops were measured at room temperature using a Lake Shore 7410 vibrating sample magnetometer (Lake Shore Cryotronics Inc., USA). The ARM demagnetization curves were obtained at room temperature using a SRM-755 SQUID magnetometer with inline ARM acquisition and AF demagnetization unit (2G Enterprises, USA).

To investigate the stability of phases with different coercivity to temperature demagnetization, an analogue to 3-axis IRM Lowrie test widely used in paleomagnetism [8] was used. Samples were given a two-component IRM in a 1T field, hard component being acquired in a 1 T field, soft — in either 0.2 or 0.35 T field. Samples were then demagnetized by heating in zero field to 700°C, 0.25 deg/s, using a vibrating sample thermomagnetometer (Orion Ltd, Russia).

To evaluate the hysteresis characteristics and anhysteretic remanent magnetization (ARM), we used the model of magnetostatically interacting single-domain particles [9,10].

3. Results and discussion

3.1. Structural characteristics
Figure 1 shows a SEM image of a sample from the Modern collection, and its elemental composition is listed in Table 1.

| No  | O   | Na  | Al  | Si  | K   | Ti  | Fe  |
|-----|-----|-----|-----|-----|-----|-----|-----|
| 145 | 51.24 | —   | —   | 48.76   | —   | —   |
| 146 | 40.08 | 0.42 | 18.82 | 25.52 | 9.84 | —   | 2.62 |
| 147 | 47.62 | 8.19 | 10.85 | 33.00 | —   | —   |
| 148 | 44.15 | 1.97 | 10.42 | 32.25 | 11.22 | —   |
| 149 | 27.38 | —   | 1.19 | 3.60   | 0.99 | 66.85 |
| 150 | 41.68 | —   | 10.24 | 20.73 | 1.41 | 0.54 | 17.49 |
| 151 | 43.31 | 0.24 | 10.20 | 31.71 | 14.54 | —   |
| 152 | 34.16 | —   | 0.16 | 0.68   | —   | 41.57 | 20.51 |
Figure 1. SEM image showing general view of MODred sample. Bright areas are predominantly iron oxides. Numbers indicate points where electron probe analyses were done.

Figure 2 shows a detailed image which yields a characteristic particle size for iron oxide phase(s).

Figure 2. SEM image of MODred sample (bright areas are mostly iron oxides).

Results of quantitative phase determination by the full-profile analysis using the Rietveld method are listed in Table 2. Iron oxides appear to be quite abundant in all samples.
Table 2. Quantitative phase analysis of samples (wt.%).

| Phase               | Val7<sup>a</sup> | MODblack<sup>b</sup> | MODred<sup>b</sup> |
|---------------------|------------------|----------------------|--------------------|
| Quartz              | 28               | 59                   | 57                 |
| Feldspars (microcline + plagioclase) | 52               | 17                   | 13                 |
| Mica                | 2                | —                    | 5                  |
| Amphibole           | —                | —                    | —                  |
| Feldspars           | 52               | 17                   | 13                 |
| Mica                | 2                | —                    | 5                  |
| Amphibole           | —                | —                    | —                  |
| Hematite            | 9                | 3                    | 6                  |
| Spinel              | 8                | 18                   | 17                 |
| Kaolin              | —                | 3                    | —                  |
| Pyroxene            | —                | —                    | 2                  |

<sup>a</sup> — the Valaam collection;
<sup>b</sup> — the Modern collection (black — inner area, red — outer area);

* $R_p = \sum y_i^{\text{obs}} - y_i^{\text{calc}} \big/ \sum y_i^{\text{obs}}$ — convergence factor of calculated and experimental X-ray profiles, $y_i$ — intensity at each experimental X-ray point.

3.2. Magnetic properties

The studied samples have quite similar hysteresis characteristics. Figure 3 shows the hysteresis loops for the samples from the Modern (MODred) and Valaam (Val7) collections respectively.

**Figure 3.** Hysteresis loop of samples from Modern (a) and Valaam (b) collections.

Hysteresis loops have a wasp-waisted shape, which suggests the presence of high-coercive and low-coercive phases. The coercive force and remanent coercivity of the MODred sample are 92.3 kA/m and 347 kA/m, respectively, remanent magnetization is 0.107 A-m<sup>2</sup>/kg. The coercive force and remanent coercivity of the sample Val7 from the Valaam collection are respectively 23.9 kA/m and 477 kA/m, remanent magnetization is 0.014 A-m<sup>2</sup>/kg.

Figure 4 show an ARM decay curve and its derivative (coercive spectrum) of the MODred sample, which allows to estimate the distribution of magnetic particles over coercivity.
A complete demagnetization does not occur at 79.8 kA/m indicating that a phase with a coercivity greater than 79.8 kA/m is present in the sample. It is consistent with the value of coercive force obtained from the hysteresis loop. ARM decay curves for MODblack and Valaam samples are similar. Ratios of natural and anhysteretic remanent magnetizations (NRM/ARM) range from 3 to 8. This suggests that natural magnetization of the samples has most likely a thermo-remanent origin [11,12].

An analysis of the structural and magnetic characteristics suggests that magnetic properties of the studied samples correspond to a two-phase system. The first phase is likely close to magnetite where iron is partially replaced by titanium, aluminum or vacancies, while the second phase has a lower saturation magnetization and higher coercivity.

Tests of temperature demagnetization of the isothermal remanent magnetization IRM obtained in weak and strong fields were carried out. This experiment is similar to Lowrie test, well known in paleomagnetic studies [8], but differs from the latter by that magnetization is measured at high temperature. Figure 5 shows the test results for the MODred and Val7 samples. Other samples yielded similar results.

The high coercive force (figure 3) and sharp drop of IRM (1 T) between 100 and 150°C suggest that ε-Fe₂O₃ might be present in these samples [4,13]. Demagnetization of IRM, obtained in smaller fields, at temperatures above 500°C indicates the presence of oxides close to magnetite. This is confirmed by X-ray diffraction data which show a significant amount of spinel phase in these samples. A relatively large residue of IRM (1 T) demagnetizing up to about 540°C for Val7 sample (figure 5b) might be related to magnetite-like particles arranged in chains. These would have higher coercivity compared to individual particles [14]. Besides, it must be noted that for this sample the field separating a magnetically soft phase from hard one was 0.2 T, rather then 0.35 T for the MODred sample.
3.3. Theoretical modeling

We now carry out a theoretical evaluation of the anhysteretic remanent magnetization $M_{ri}$ and hysteresis characteristics ($M_s$ is the saturation magnetization and $M_{rs}$ is the remanent saturation magnetization) following the approach outlined in [6,7].

Let us consider strongly and weakly magnetic phases jointly as clusters of magnetostatically interacting grains and evaluate the contribution of both phases to hysteresis characteristics of the studied samples. The contribution of high-coercive phase to anhysteretic remanent magnetization is not taken into account, since maximum amplitude of the alternating field (80 kA/m) is most likely less than the coercive force of the $\varepsilon$-Fe$_2$O$_3$ phase.

In SEM images (figure 1), it is seen that light regions which are predominantly iron oxides make up less than 1% by volume. In a first approximation, one can replace the saturation magnetization ($M_s = cI_s$) by the maximum magnetization value (figure 3) and estimate the volume concentration $c$ and the spontaneous magnetization $I_s$ of the material determining the hysteresis properties.

In further calculations, we take the spontaneous magnetization of a strongly magnetic phase equal to 480 kA/m and that of a weakly magnetic phase to 100 kA/m [1]. $\varepsilon$-Fe$_2$O$_3$ particles have a characteristic size of 30 nm. If this size is exceeded, the crystal structure transforms into $\alpha$-Fe$_2$O$_3$ due to lower surface energy of the latter [1]. Single-domain particles of a phase close to magnetite have a characteristic size of the order of 20-30 nm. Particle clusters have a size of about 2 μm as seen in figure 2.

Let us calculate the remanent magnetization of a system of clusters consisting of interacting particles having spontaneous magnetization $I_s$. The volume concentration $c = c_{cl}\eta$, where $c_{cl}$ and $\eta$ are the concentrations of clusters and particles in clusters respectively.

Relative remanent saturation magnetization is then written as follows [7]

$$
\zeta_1 = \frac{1}{3} \left[ \frac{1}{2} \left[ \gamma_1 H_2 (x_0) - \frac{\gamma_2}{12} H_{13} (x_0) - \frac{\gamma_3}{36} H_5 (x_0) \right] \right],
$$

where $x_0$ — an intensity of a dimensionless random interaction field; $\phi_n(x_0)$ — density of the normal distribution function; $\gamma_1$ — asymmetry; $\gamma_2$ — excess; $H_2, H_3, H_5$ — Hermite polynomials of 2nd, 3rd and 5th order respectively.

Experimental relative remanent saturation magnetization can be written as:

$$
\zeta_2 = \frac{M_{rs}}{\eta I_s},
$$

where $M_{rs}$ — an experimental value of the remanent saturation magnetization.

We then plot in Figure 6 dependences of $\zeta_1$ and $\zeta_2$ on $I_s$ using relations (1) and (2).

![Figure 6](image-url)

**Figure 6.** The curves of dependence of $\zeta_1$ and $\zeta_2$ on $I_s$ for MODred: magnetite-like (a) and $\varepsilon$-Fe$_2$O$_3$ (b) phases.
The intersection point of the curves will correspond to the spontaneous magnetization of the particles contributing to the remanent magnetization. The concentration of particles in clusters $\eta$ was taken in the range of 10-25%.

The saturation magnetization and the remanent saturation magnetization of a two-phase system are equal to

$$M_s = c_1 I_s 1 + c_2 I_s 2,$$

$$M_{rs} = c_1 x_1 I_s 1 + c_2 x_2 I_s 2,$$

where $I_s 1$ and $I_s 2$ — spontaneous magnetizations; $c_1$ and $c_2$ — concentrations; $x_1$ and $x_2$ — contributions to remanent magnetization (separately from each phase) of magnetite and $\varepsilon$-Fe$_2$O$_3$ particles respectively.

We then estimate the ARM as [6]

$$M_{rs} = \frac{1}{3} c_d \eta I_s \frac{H}{H_{\text{max}}},$$

where $c_d$ — volume fraction of clusters; $\eta$ — fraction of particles in a cluster; $I_s$ — spontaneous magnetization; $H$ — external constant ARM magnetizing field (equal to 80 A/m); $H_{\text{max}}$ — maximum interaction field ($H_{\text{max}} \approx 5 c I_s$, $c = c_d \eta$).

Since natural remanent magnetization is not completely erased in maximum at field available to us (figure 4a), the concentration of high-coercive particles can be higher than calculated.

The best approximation to the experiment shows the presence of a strongly and weakly magnetic phase (magnetite-like and $\varepsilon$-Fe$_2$O$_3$) in a ratio of 1:9. In this case, their concentrations would be respectively $c_1 = 4 \times 10^{-4}$ and $c_2 = 36 \times 10^{-4}$. The fraction of particles $(x_1, x_2)$ contributing to the remanent saturation magnetization was $x_1, x_2 \approx 30\%$ of each phase (3).

4. Conclusion

In this work, an experimental and theoretical study of the structure and magnetic properties of fired clay samples is carried out. An analysis of experimental and published data allows us to conclude that the samples contain a large amount of iron oxides, possibly including highly coercive $\varepsilon$-Fe$_2$O$_3$ nanoparticles. Theoretical modeling is in a good agreement with experimental data dividing the magnetic material into two components present in the ratio of about 1:9: (1) “low coercive strongly magnetic” phase close to magnetite and (2) “high coercive weakly magnetic” close to epsilon iron (III) oxide. Chains of magnetite-like grains may be part of a high coercivity phase.

The results obtained are in a good agreement to published data [1] in what concerns the stabilization of $\varepsilon$-Fe$_2$O$_3$ nanoparticles due to a matrix of silicates.

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