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EFFECT OF THERMAL TREATMENT ON THE MAGNETIC PROPERTIES OF CERAMIC SAMPLES FROM EASTERN ROMANIA CLAY DEPOSITS

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The ancient pottery can reveal an important amount of information regarding the civilizations which have produced and used it. Magnetic measurements (MHL and FORC) combined with SEM and XRD investigation of the samples collected from archaeological sites are efficient tool for gathering an important part of this information. We have systematically recreated in the laboratory procedures of pottery fabrication for comparing the results with the archaeological material gathered from the Cucuteni culture. Different magnetic properties of the samples are induced by thermal treatment of raw clays used for pottery during firing process. The purpose of this work is to clarify the connection between firing parameters (temperature and firing duration) and to understand their influence on the magnetic properties of the samples. The coercivity and saturation magnetization measured on the major hysteresis loops were studied as a function of temperature and duration of the treatment. This behaviour could be linked with the formation of new iron oxides phases at different temperatures which has been confirmed by SEM and XRD analysis. These changes of the magnetic properties with treatment temperature are important for establishing firing conditions of the ancient pottery collected from archaeological sites.

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Keywords: FORC diagram, Cucuteni culture, clay samples

1. Introduction

Magnetic properties studies of ancient ceramics are based on the assumptions that pottery produced from a specific clay source will show similar characteristics which will be distinct from that of pottery produced from different clay. Hence, pottery can be attributed to particular technological and provenance groups, which can be then correlated with their specific origin. Usually, the natural clay, if prepared alone, is not adequate to produce a good quality clay paste. The ancient techniques for producing pottery are, for example, levigation, tempering with non-plastic additives and/or the mixing of different clay types [1]. However, although the pottery production process involves complex human behavioural patterns, it is still the clay source characteristics that influence essentially the magnetic properties of the ceramics. We assume, therefore, that an examination of the magnetic properties of different clay types from Eastern Moldavia may help to form a better understanding of the magnetic properties characteristics specific to Cucuteni pottery. The present study focuses on thermal treatment of clay sampled from the nearby area of the eponymous site of the Cucuteni Chalcolithic culture. The Cucuteni culture represents the eastern part of the Cucuteni-Trypillia civilization which developed during the V-IVth millennia (4600-3700 cal B.C.) covering large parts of the Romania, Ukraine and the Republic of Moldova present-day territory.

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The site is located on a small hill plateau known as *Cetătuie*. This was separated from the eastern side of the large Laiu Plateau and bordered by steep slopes on three sides, south, east and north. The settlement is situated on top of a structural plateau on the right side of the Valea Oii stream, dominating the entire region, both to the east, north and south.

Due to the linear flow the southern slope has modified gaining the appearance of ravines. The erosion contributed to a deep incision which highlighted the clay deposits in the sandstone sequence specific to the structural plateaus of Northern Moldavia. The geological succession in the archaeological site area is composed of intercalations of clays, sands and sandstones, with two levels of oolitic and specific associated fossil fauna.

2. Experimental

The magnetic analysis of clay samples using major hysteresis loop is possible because most of the pottery contains iron oxide compounds which are ferro/ferri magnetic in different phases.

2.1. Sample preparation

Clay used for sample preparation has been collected from the neighbouring area of the Cucuteni culture eponymous site. The clay has been mixed with distilled water, thoroughly homogenized, moulded in 8 mm thick sheet and dried in free air. Samples used for firing have been obtained by cutting pieces having 8 x 8 x 12 mm from the dried clay sheet. These samples have been fired directly in two electric furnaces at different temperatures and durations as presented in table 1.

Table 1. List of samples obtained by firing clay

Sample Name	Firing temperature (ºC)	Firing time (hours)	Furnace
E1	700	1.0	C2 (home made)
E2	700	3.0	
E3	700	6.0	
E4	750	3.0	
E5	750	6.0	
E6	750	1.0	
E7	650	3.0	
E8	650	6.0	
E9	650	1.0	
E10	600	6.0	
E11	600	3.0	
E12	600	1.0	
EA0	1200	0.5	Nabertherm
EA1	900	0.5	
EA2	950	0.5	
EA3	1000	0.5	
EA4	1050	0.5	
EA5	850	0.5	
EA6	800	0.5	
EA7	750	0.5	
EA8	700	0.5	
EA9	650	0.5	
EA10	600	0.5	
EA11	1100	0.5	
EA12	1150	0.5	

Sample Name	Firing temperature (ºC)	Firing time (hours)	Furnace
EA13	550	0.5	
EA14	500	0.5	
EA15	450	0.5	
EA16	400	0.5	
EA17	350	0.5	
EA18	300	0.5	

Samples used for Scanning Electron Microscope (SEM) have been obtained by breaking a small part from each fired sample, trying to obtain a flat surface of the sample followed by deposition of 10 nm thickness thin layer of chromium. Samples used for XRD has been produced by transforming a part of each fired sample into powder. Samples used for VSM (Vibrating Sample Magnetometer) have been prepared by cutting from each fired sample a small quantity (between 20 and 30 mg) which has been transformed into powder and pressed in capsules for mounting on the head of a Vibrating Magnetometer Sample (VSM). Each capsule has been weighted before and after filling with powder, using a high precision electronic balance having 0.01 mg last digit. The mass of each sample has been calculated by subtracting mass of the empty capsule from the mass of the filled capsule. All VSM samples are listed in the table 2.

Table 2. List of the VSM samples.

Sample name	Firing temperature (ºC)	Firing time (hours)	Mass (mg)	Furnace
E1-1	700	1.0	29.48	C2 (home made)
E2-1	700	3.0	20.92	
E3-1	700	6.0	31.18	
E4-1	750	3.0	25.91	
E5-1	750	6.0	29.39	
E6-1	750	1.0	25.22	
E7-1	650	3.0	26.82	
E8-1	650	6.0	30.56	
E9-1	650	1.0	25.96	
E10-1	600	6.0	24.52	
E11-1	600	3.0	20.08	
E12-1	600	1.0	23.64	
EA0-1	1200	0.5	71.83	Nabertherm
EA1-1	900	0.5	24.19	
EA2-1	950	0.5	18.72	
EA3-1	1000	0.5	30.81	
EA4-1	1050	0.5	27.47	
EA5-1	850	0.5	24.25	
EA6-1	800	0.5	28.06	
EA7-1	750	0.5	27.3	
EA8-1	700	0.5	28.32	
EA9-1	650	0.5	23.75	

Sample name	Firing temperature (ºC)	Firing time (hours)	Mass (mg)	Furnace
EA10-1	600	0.5	20.78	
EA11-1	1100	0.5	34.81	
EA12-1	1150	0.5	21.40	
EA13-1	550	0.5	23.65	
EA14-1	500	0.5	28.99	
EA15-1	450	0.5	34.45	
EA16-1	400	0.5	35.90	
EA17-1	350	0.5	29.24	
EA18-1	300	0.5	24.11	

2.2. Methods used for studying the samples

Samples have been heated until they have reached the firing temperature which has been maintained constant for the entire duration of the treatment followed by cooling down to the room temperature. The heating rate has been kept the same for all samples (0.15ºC/s) and the cooling rate was the same for all samples (0.3ºC/s). Two electric furnaces have been used for this purpose. One of them is Nabertherm model LHT 406GN2GS having maximum heating power of 5.2 kW which allows to fire samples up to 1600ºC and has been used for firing samples EA0 to EA18 at temperatures between 300ºC and 1200ºC with 50ºC step for 0.5 hours. The other furnace (C2) was a home made one and has been used for samples E0 to E12 which have been fired at temperatures between 600ºC and 750ºC with 50ºC step for 1, 3 and 6 hours.

Three methods for analysing the samples have been used: magnetic analysis using a Dual Princeton Measurements MicroMag^{TM} 2900/3900 AGM/VSM, Vibrating Sample Magnetometer (VSM), Scanning Electron Microscopy (SEM) using Hitachi S-3400N scanning electron microscope and XRD (X-Ray Diffraction) using Shimadzu LabX XRD 6000 diffractometer.

Magnetic analysis method consists in measuring magnetic moment at room temperature for a DC applied magnetic field having intensity between – 3000 Oe and +3000 Oe obtaining the Major Hysteresis Loop (MHL). Magnetic interactions profile of the samples has been obtained by performing a First-Order Reversal Curves (FORC) scan. These magnetic analysis performed provides more information than other magnetic analysis methods such magnetic susceptibility measurements [2] and proves to be an important tool for investigating clay samples.

The SEM images were obtained in the range of 2 to 500 μm using 100 to 21000 magnification, 8 to 30 kV accelerating voltage, 82 μA emission current working in SE and BSE mode.

XRD investigations have been performed using A-45-Cu X ray tube with a Cu Kα target and 40 kV for high voltage value and 30 mA for the anodic current. The range of angles used was 2θ between 4 – 40º with a step of 0.02º and a scanning speed of 2º/min.

This combination of magnetic analysis method with other non magnetic methods such as XRD and SEM applied to the fired clay samples or to different categories of ancient ceramic samples [3] has been used for improving the accuracy of the information about firing conditions of the ancient pottery.

3. Results

In Figure 1 is presented the major hysteretic loops (MHL) for the samples (EAx) treated for 0.5 hours at different temperatures. (Figure. 1)

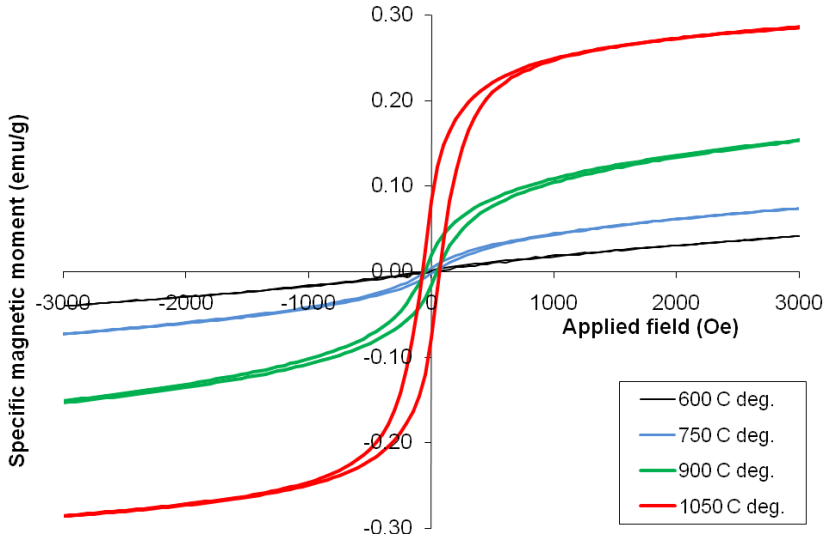


Fig. 1. Major hysteretic loops for clay samples after treatment at different temperatures and for 0.5 hours

By comparing major hysteresis loops for samples treated at the same temperature (750ºC) but for different times, different coercivities and saturation moments size have been found like it appears on MHL from Figure 2.

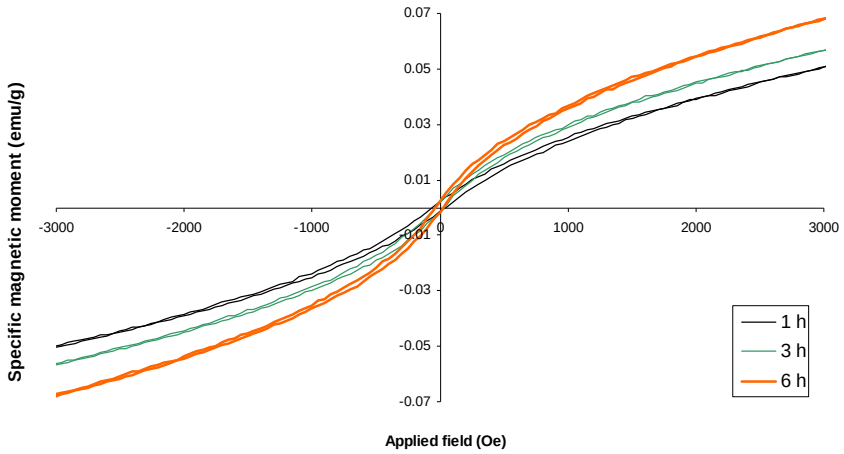


Fig. 2. Major hysteresis loops for clay samples after treatment for different durations at 750ºC.

The coercive field versus temperature is presented in Fig. 3.

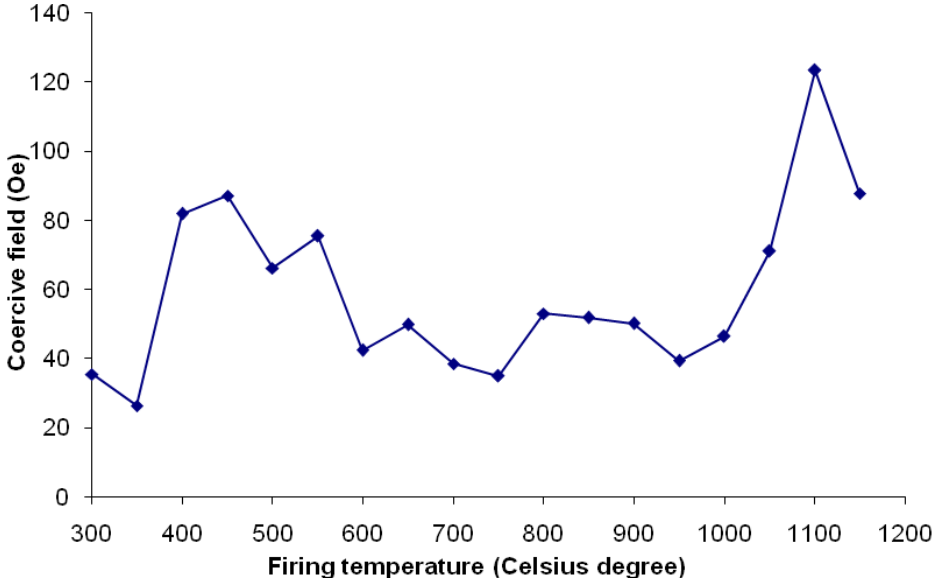


Fig. 3. Variation of the coercive field with firing temperature.

Plotting the value of the saturation moment with firing temperature for EA0-EA-18 samples a systematic rising of its value as in Figure 4 has been observed.

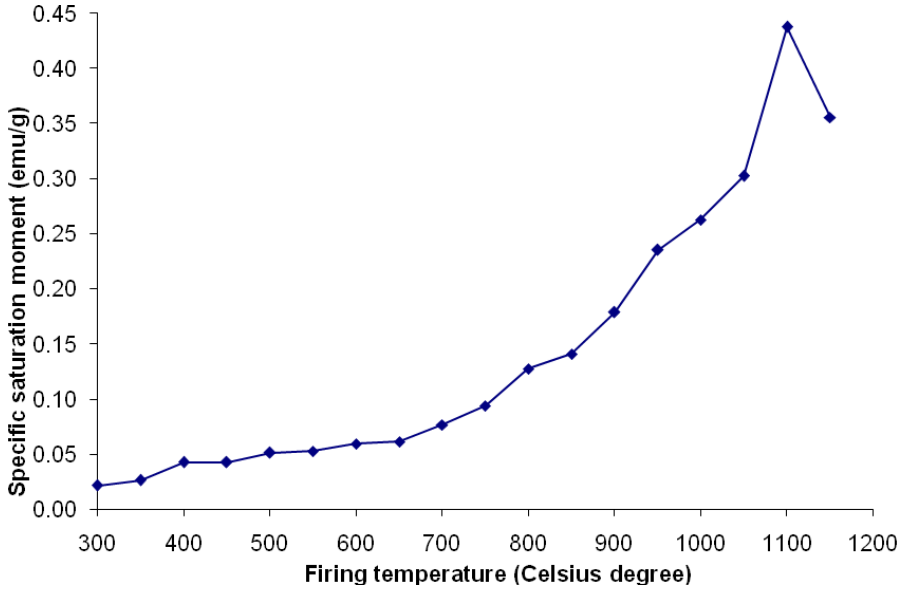
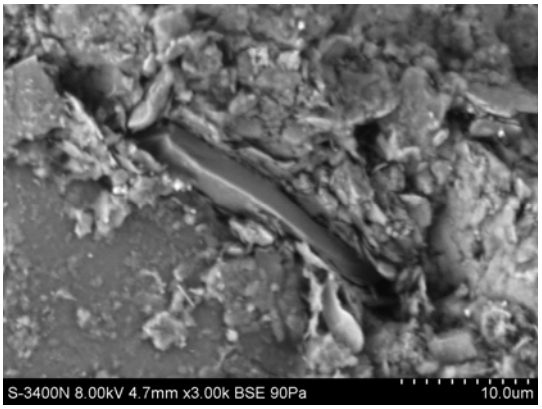
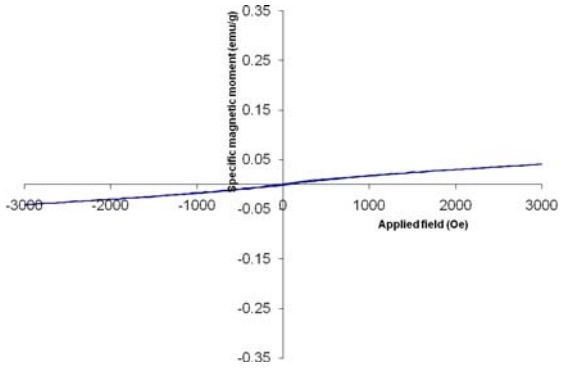


Fig. 4. Variation of the specific saturation moment with firing temperature.

Images obtained using SEM for samples fired at 600ºC, 850ºC, 1100ºC and 1150ºC are presented in the Figures 5 – 7 together with corresponding magnetic hysteresis cycle for each of EA10, EA5 and EA12 samples.

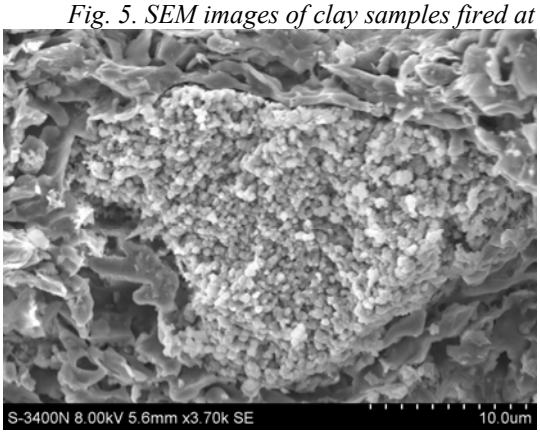


(a)

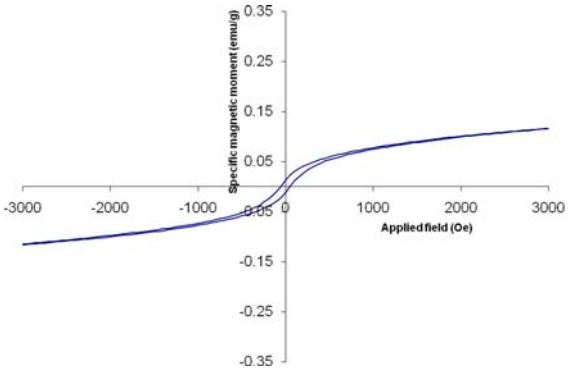


(b)

Fig. 5. SEM images of clay samples fired at 600ºC (EA10) (a) and corresponding hysteresis cycle (b)

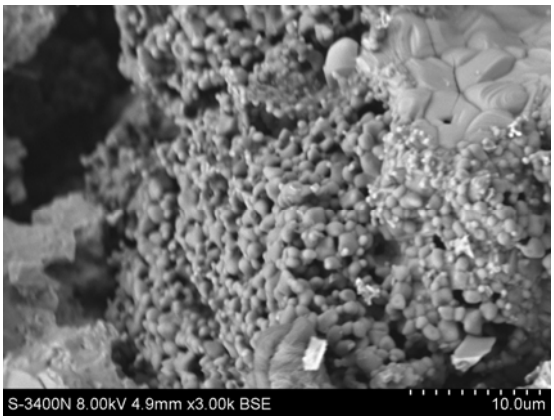


(a)

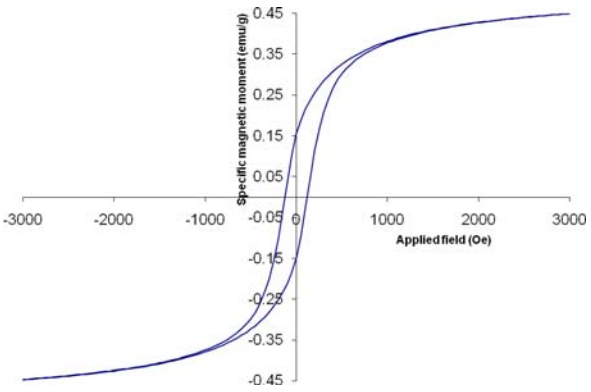


(b)

Fig.6. SEM images of clay samples fired at 850ºC (EA5) (a) and corresponding hysteresis cycle (b)

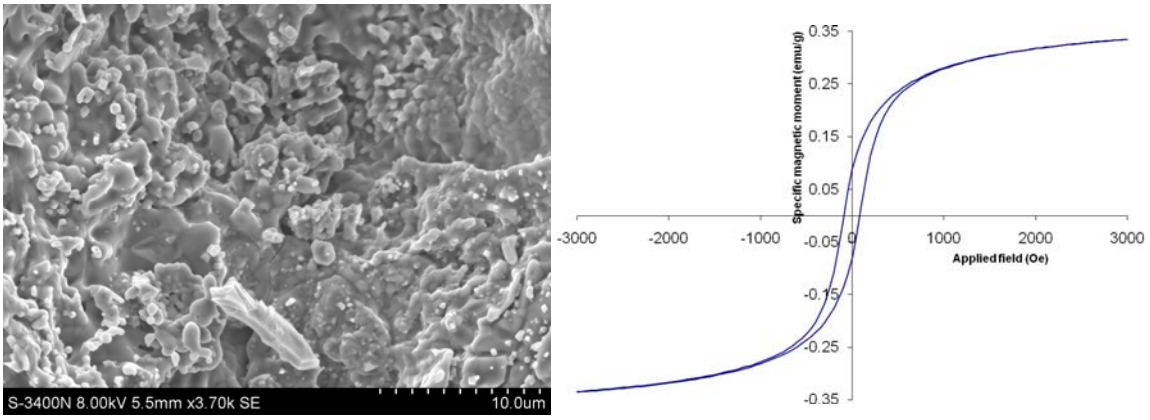


(a)



(b)

Fig.7. SEM images of clay samples fired at 1100ºC (EA11)(a) and corresponding hysteresis cycle (b)



(a) (b)

Fig.8. SEM images of clay samples fired at 1150ºC (EA12)(a) and corresponding hysteresis cycle (b)

For the sample EA11 we have also measured a set of first-order reversal curves (FORC) (see Fig. 9). This type of experimental procedure was designed by Mayergoyz as identification technique for the well-known Classical Preisach Model (CPM) [4]. Pike and collaborators, in 1999, [5] have motivated the use of this method as a purely experimental technique with virtually no link with CPM. The measurement on a first-order reversal curve is starting on one branch of the major hysteresis loop (MHL) at a field called reversal field, H_r. When the applied field on the FORC starting in H_r is H the value of the measured moment is a function of both H_r and H (Figure 9). The FORC distribution is calculated as the second order mixed derivative of the moment and is given by: $\rho(H,H_r)=-(1/2)\left(\partial^2 m/\partial H\partial H_r\right)$. This distribution, experimentally calculated is closely related to the actual Preisach distribution of the sample. To understand the relation between the two distributions we mention that the fields (H,H_r) correspond to the characteristic switching fields (H_α,H_β) of the rectangular Preisach hysterons. Using these switching fields one can calculate the coercive field of the hysterons $H_c=(1/2)(H-H_r)$ and the interaction field, $H_i=-(1/2)(H+H_r)$ [6], [7]. The contour plot of the FORC distribution is usually called FORC diagram. In Figure 10 one shows the experimental FORC diagram for the mentioned sample. This method shows the distribution of coercivities of the ferro/ferri magnetic particles in the sample. The use of this method was first proposed in [8] and offers the opportunity for accurate account for the distribution of hysteretic entities in ceramic samples. In Figure10 we also show the coercive and interaction fields distributions as obtained from the FORC diagram along two sections (one along the interaction field line and one along the coercivity line). The two lines were centred in the point of most probable coercivity, at 128 Oe.

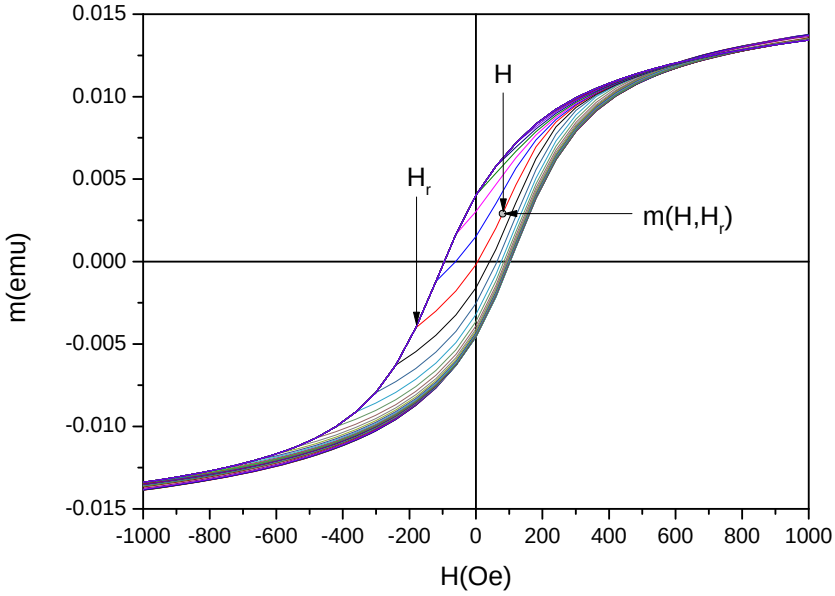


Fig. 9. FORC analysis for EA11-1 sample (0.03481g).

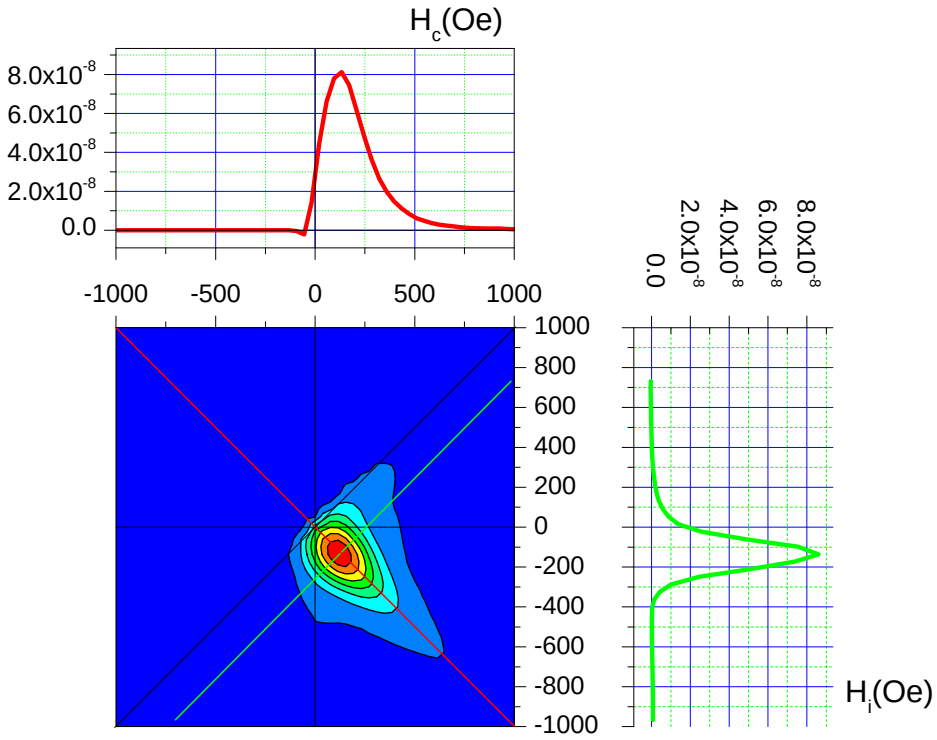


Fig. 10. The coercive and interaction fields distributions as obtained from the FORC diagram, Hc_{max} = 128 Oe

The diffractograms for samples fired at 600ºC , 850ºC , 1100ºC and 1150ºC are shown in Figure 11.

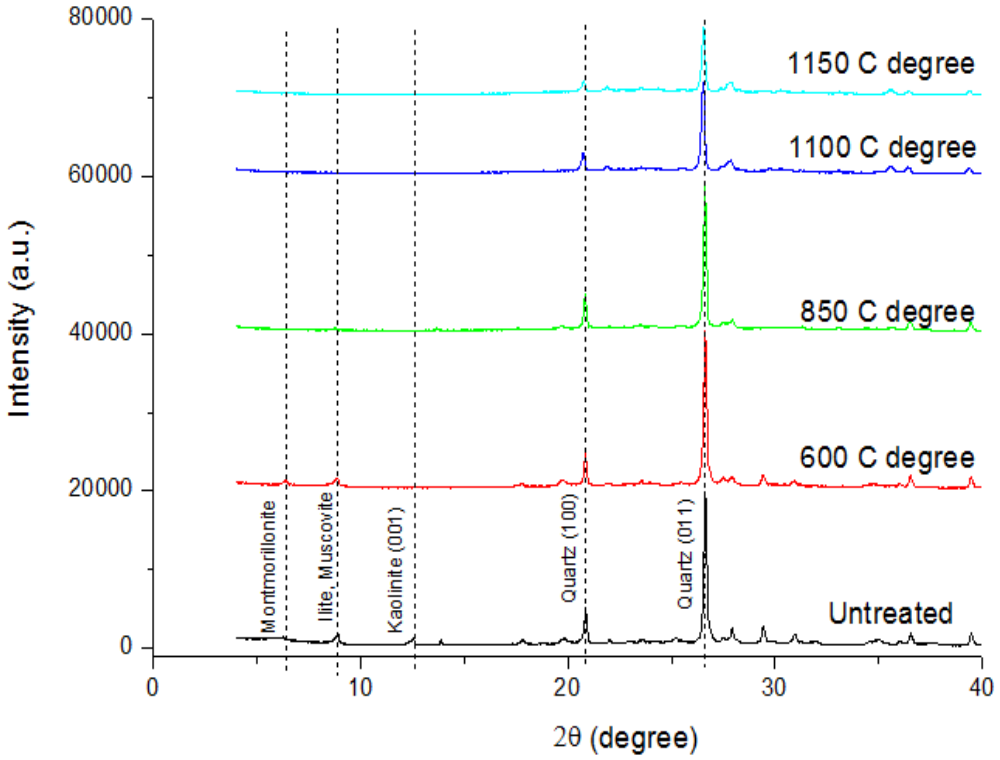


Fig.11. Comparison of the XRD pattern analysis of clay samples fired at 600, 850, 1100 and 1150ºC

4. Discussion

For samples treated for 0.5 h at different temperatures a clear difference between hysteresis loops appears. There is a clear rise of the values of the saturation magnetic moment (Figure 1) which is more visible in Figure 4. We have noticed that in the temperature range of 350 –1100ºC there is a rise of the specific saturation moment. For the sample fired at 1200ºC we observed a slight drop of the specific saturation moment comparing with the sample fired at 1150ºC.

These differences observed for the specific magnetization values could be related to the structural phases which appeared due to the firing process

It is proposed that the magnetic and microstructural data from the laboratory clay heated samples may be used as a comparative method to analyse archaeological pottery samples, discovered within the proximity of the selected clay source, in order to reveal the pottery samples previous thermal history.

Some of the authors referring to ancient ceramics consider that large and distorted loop corresponds to a combination of magnetite, hematite, maghemite and goethite [3].

These MHL shapes and sizes are due to phases change of magnetic compounds with temperature rising. The literature mentions that for unheated sample or heated bellow 250ºC iron appears usually as iron oxyhydroxide, which is included most of the time in goethite. If firing temperature is increased in (300ºC – 600ºC) range, goethite transforms in hematite [9] which becomes completely crystallized above 750ºC [10] and is decreasing over 1000ºC.

Kaolinite and illite are also present in the analysed clay samples. In general, they are transformed in mullite at high firing temperature, over 700ºC [11]. On higher temperatures quartz is dominant and is slightly decreasing with temperature rising. Formation of new phases at different temperatures can be seen in SEM images.

Images for EA10 sample which has been treated at 600ºC show a lamellar morphology. They appear like lamellae conglomerates (Figure 5). Kaolinite which has been found in the untreated samples has disappeared at 600ºC.

Increasing firing temperature up to 850^0 C will produce formation of small particles (about 300 nm in diameter) which are in some area agglomerated together or spread between larger particles (Figure 6) and also shows the formation of larger particles.

On higher temperatures (1100ºC) small particles are still present (about 300nm in diameter) as it is shown in Figure 7 but larger particles are formed too (1-2 μm in diameter). At this temperature signs of vitrification are present. By increasing temperature up to 1150ºC vitrification is dominant in most part of the volume of EA12 sample (Figure 8). Crystals with size between 300 nm and 2 μm are present on samples treated on temperatures between 850ºC and 1100ºC.

At temperatures greater than 1000ºC appears a reduction of porosity and contraction of the samples mass due to formation of the glassy phase which is gradually filling the pores [11].

These results are confirmed also by the results obtained in the XRD analysis. Kaolinite which initially were present in the untreated clay sample [12] [13] is disappearing on 600ºC, illite and muscovite presence is decreasing with temperature rising to 850ºC and is disappearing above this value. Montmorillonite [14] which was present on samples treated at 600ºC is disappearing at 850ºC and above this value. Quartz is present in all samples [15] and is reaching a maximum on samples treated at 600ºC and 850ºC and is reduced gradually at temperatures above this value followed by an important decrease above 1100ºC [16].

The method presented above has the advantage that requires less magnetic measurements volume than the method proposed by Linford and Platzman [18] which have done an analysis of hysteresis data combined with IRM analysis for establishing an algorithm for estimating the firing temperature of archaeological sediments. There they combined a larger number of measured characteristics of the samples such as mass susceptibility, saturation magnetisation, saturation remanence, coercive force, coercivity of remanence.

5. Conclusions

Phase changes due to increasing the firing temperature in the clay samples have been observed on XRD analysis and are correlated with magnetic behaviour of the samples. The specific saturation magnetic moment increases with temperature significantly towards values higher than 650ºC and the coercive field has a periodic variation with smaller amplitude in 400 – 1000ºC range.

This combination of methods can be applied also on stone thermal weathering [9] [19] if that stone contains iron compounds [17]. By combining the magnetic MHL and FORC to SEM and XRD analysis, the accuracy of determining the firing temperature of the pottery samples will be improved and will become an important tool in archaeology. For improving the efficiency of this method is necessary to create a database for clays having different compositions from different areas of the Cucuteni culture.

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