EGU General Assembly 2020

Influence of firing conditions on the rock magnetic properties

Preliminary results from experimental heating experiments

Petar Dimitrov[1, 2], Maria Kostadinova-Avramova[1], Andrei Kosterov[3], Deyan Lesigyarski[1]

NIGGG

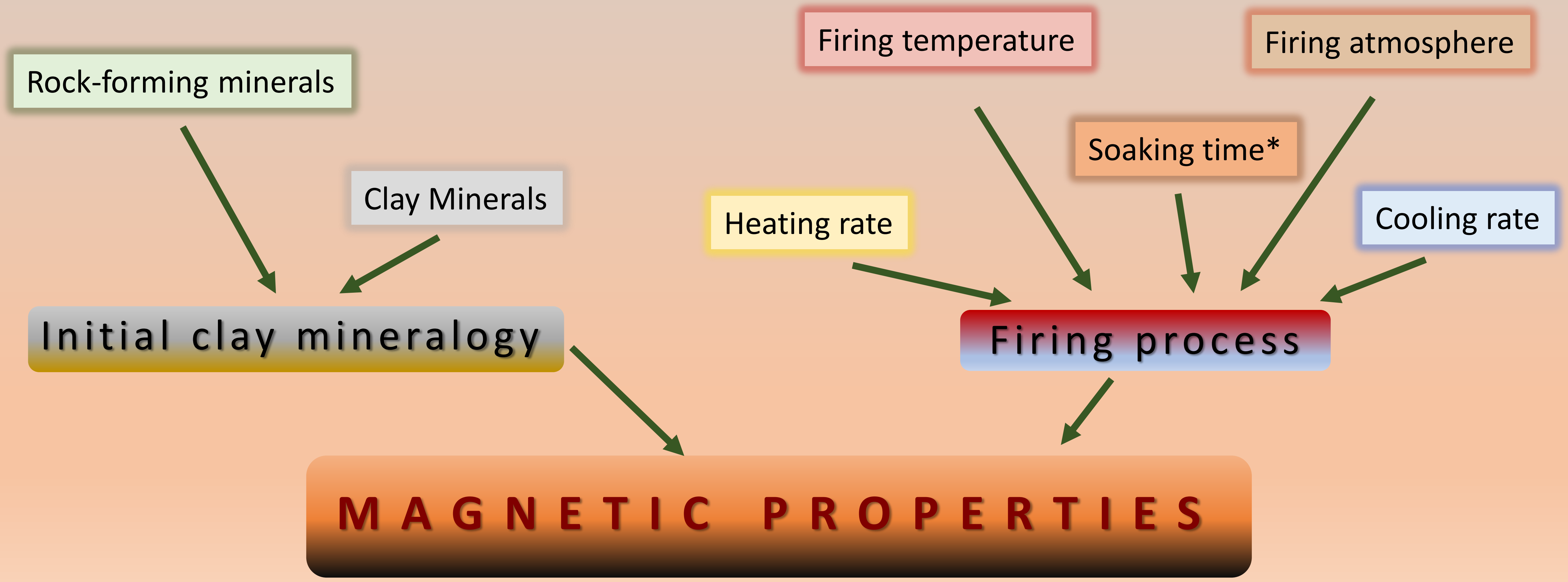
[1]National Institute of Geophysics, Geodesy and Geography, Sofia, Bulgaria (miki4740@abv.bg; dekemvri_14@abv.bg)
[2]National Archaeological Institute with Museum, Sofia, Bulgaria (p_d_dimitrov@abv.bg)
[3]St. Petersburg State University, St. Petersburg, Russia (a.kosterov@spbu.ru)

St. Petersburg University

1892 - 1921 - 1948

Archaeomagnetism is successfully applied in many geophysical and archaeological researches. The effectiveness of this method is highly influenced by the magnetic properties of the materials studied – various burnt clay objects.

The magnetic mineralogy complexity of burnt clay is predetermined by a complex interaction of various factors



* "Soaking time" is used as "the time of exposure to temperatures" according to *Livingstone Smith (2001)*

Experimental archaeology has enormous potential for:

- proving various archaeological statements and assumptions
- clarifying important details of ancient firing technologies
- improving the accuracy of the modern interdisciplinary research methods

Three combustion structures were constructed and several experimental firings were performed in each of them in order to accumulate more data about the processes of firing and cooling. Cubic samples prepared from different clay types were subjected to these firings and the resulting magnetic properties after the first and the forth heating/cooling cycle were studied.

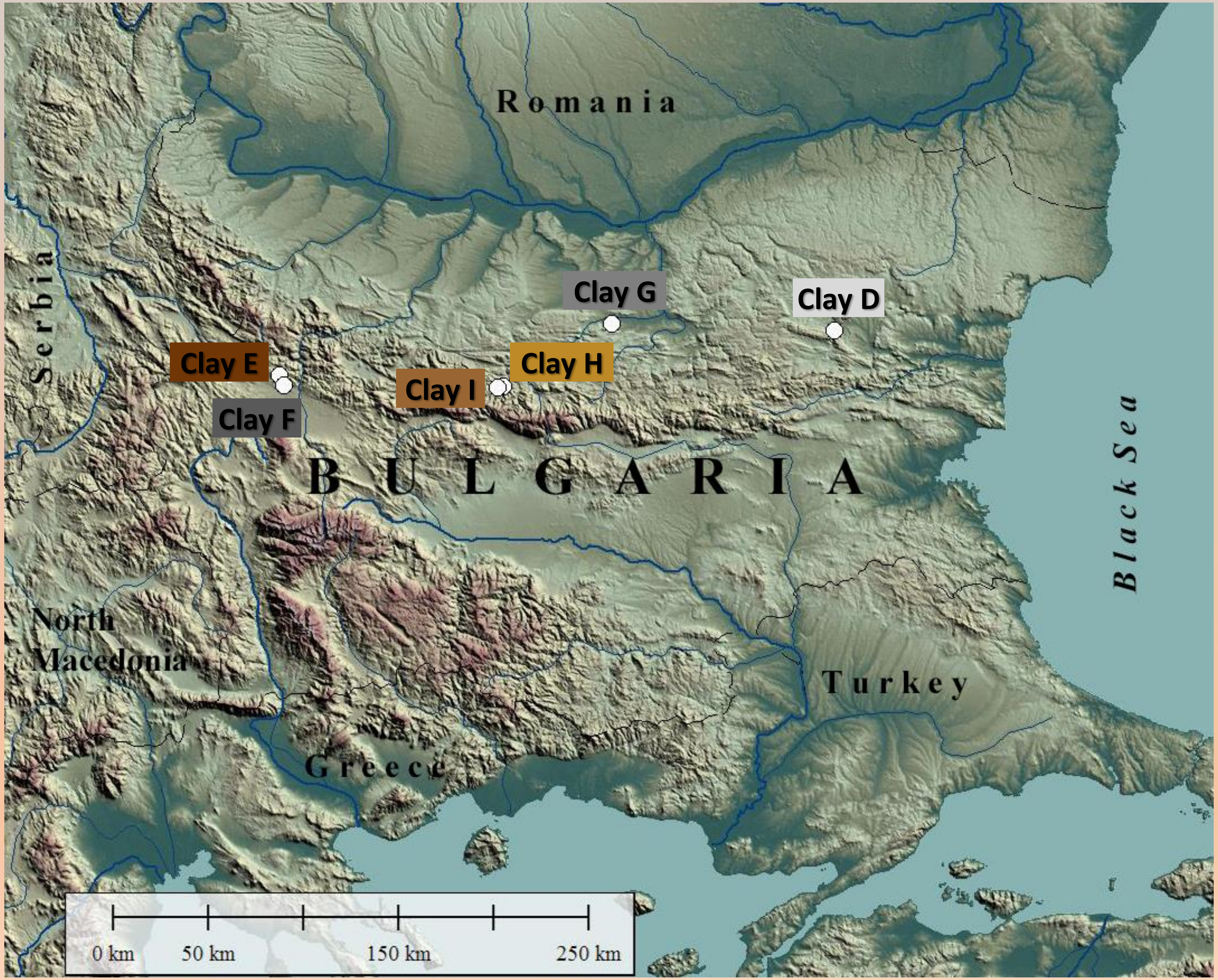
Open hearth

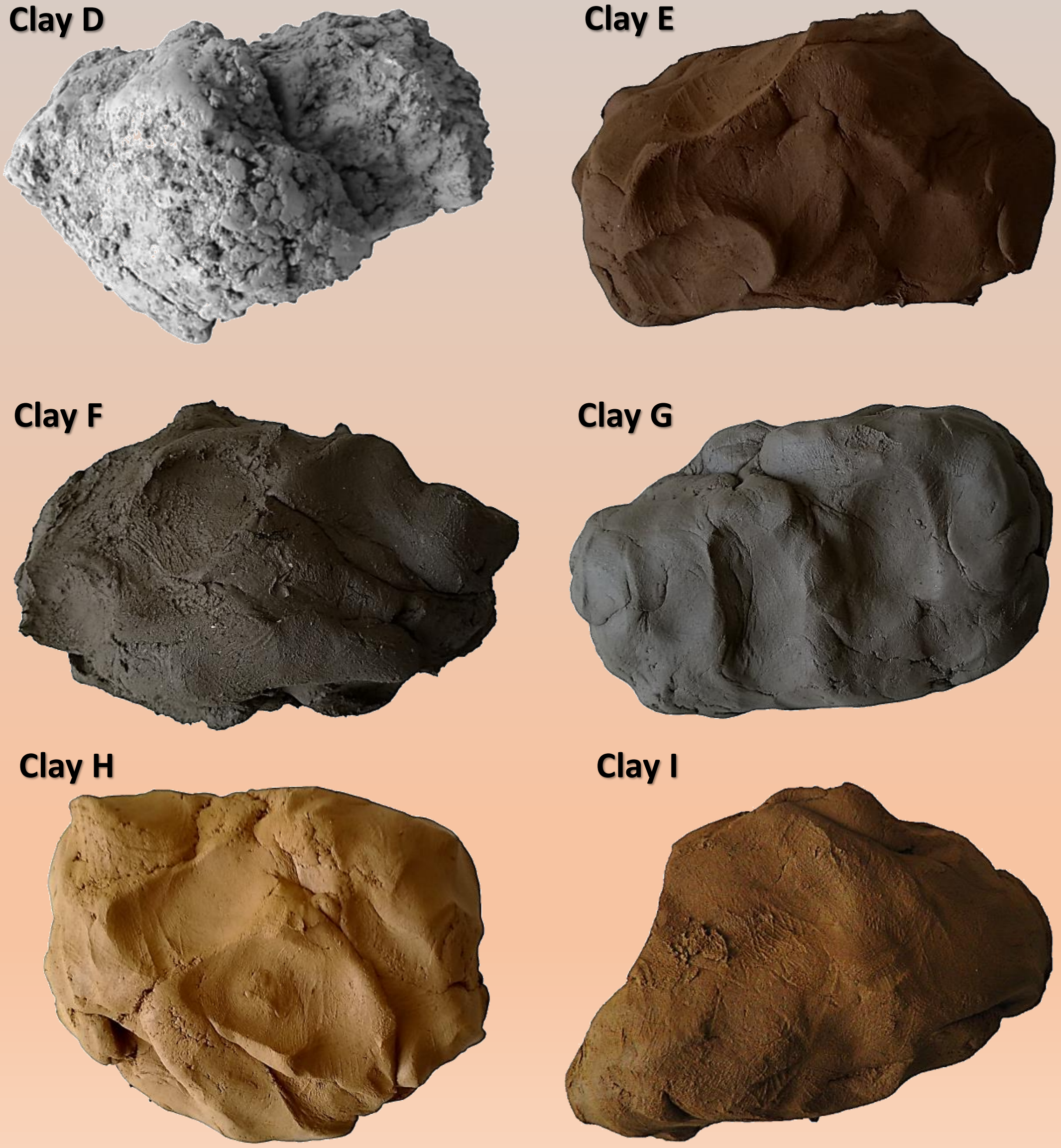
Single-chamber furnace

Double-chamber kiln

All clay deposits are located in the Northern part of Bulgaria

Clays **E**, **F**, **H** and **I** are from mountainous regions where metamorphic rocks dominate but clays **D** and **G** are from the Danube plain associated with the Quaternary loess accumulations. Therefore, different sources of rock-forming minerals can be suggested.





Non-magnetic data

Grain-size analysis were carried out in the Central Research Laboratory of Geochemistry – University of Mining and Geology, Sofia

Grain-size distributions for the different clays in mm						
Clay	> 2	2 – 0.063	0.063 – 0.02	0.02 – 0.0063	0.0063 – 0.002	< 0.002
D	1 %	0 %	14 %	34%	26 %	25 %
E	0 %	12 %	13 %	12 %	9 %	54 %
F	0 %	2 %	21 %	30 %	23 %	22 %
G	0 %	2 %	11 %	29 %	21 %	35 %
H	0 %	2 %	11 %	29 %	21 %	43 %
I	1 %	5 %	13 %	22 %	13 %	46 %

X-Ray diffraction were performed independently in: 1) Laboratory of X-ray Diffraction Analysis, Institute of mineralogy and crystallography, Bulgarian Academy of Science and 2) Centre for X-ray Diffraction Studies, St. Petersburg University Research Park (https://researchpark.spbu.ru/en/xrd-eng). The same model of Powder X-ray diffractometer D2 Phaser (Bruker AXS) was used.

Clay	Detrital (rock-forming) minerals	Secondary (clay) minerals
D	quartz, albite, muscovite, calcite	Na-montmorillonite, kaolinite, clinochlore
E	quartz, muscovite, potassium feldspar	Al-montmorillonite
F	quartz, albite, mica, calcite, perovskite	Al-montmorillonite, kaolinite
G	quartz, muscovite, calcite	Na-montmorillonite, kaolinite, clinochlore
H	quartz, albite, mica, potassium feldspar	Al-montmorillonite, kaolinite
I	quartz, albite, mica	Al-montmorillonite, kaolinite

X-Ray fluorescence analysis were done using portable device SI TITAN 800 (Bruker, Germany)

Element	Clay D	Clay E	Clay F	Clay G	Clay H	Clay I	RSD_m
MgO, %	3,19 ± 1,09	3,65 ± 1,08	2,04 ± 0,95	2,60 ± 1,08	2,58 ± 1,01	2,83 ± 0,97	*36,8*
Al_2O_3, %	22,55 ± 0,59	27,60 ± 0,65	20,18 ± 0,55	22,52 ± 0,59	25,01 ± 0,61	25,62 ± 0,62	*2,5*
SiO_2, %	48,73 ± 0,60	54,30 ± 0,64	55,58 ± 0,65	57,96 ± 0,68	67,89 ± 0,74	62,73 ± 0,70	*1,1*
P_2O_5, %	0,12 ± 0,05	0,09 ± 0,03	0,11 ± 0,04	0,16 ± 0,04	0,08 ± 0,03	0,06 ± 0,03	*36,6*
S, %	0,25 ± 0,02	< 0,01	0,18 ± 0,02	0,13 ± 0,02	0,06 ± 0,02	< 0,01	*10,9*
K_2O, %	3,46 ± 0,04	3,25 ± 0,04	2,39 ± 0,03	3,00 ± 0,04	2,98 ± 0,04	2,89 ± 0,04	*1,2*
CaO, %	12,33 ± 0,07	1,45 ± 0,03	7,91 ± 0,05	11,03 ± 0,06	0,82 ± 0,02	0,70 ± 0,02	*1,2*
TiO_2, %	0,68 ± 0,02	0,50 ± 0,01	0,66 ± 0,01	0,66 ± 0,01	0,62 ± 0,01	0,66 ± 0,01	*2,2*
MnO, %	0,076 ± 0,010	0,290 ± 0,016	0,039 ± 0,008	0,091 ± 0,011	0,074 ± 0,009	0,044 ± 0,008	*13,0*
Fe_2O_3, %	5,83 ± 0,06	7,83 ± 0,06	4,69 ± 0,05	5,43 ± 0,06	5,46 ± 0,05	6,17 ± 0,06	*1,0*
V, ppm	121 ± 39	142 ± 31	130 ± 33	108 ± 33	88 ± 19	111 ± 24	*23,6*
Cr, ppm	76 ± 31	101 ± 31	57 ± 28	80 ± 30	88 ± 28	79 ± 29	*37,1*
Ni, ppm	< 10	40 ± 22	< 10	< 10	< 10	< 10	*55,0*
Cu, ppm	52 ± 13	37 ± 9	53 ± 12	46 ± 12	38 ± 9	38 ± 9	*24,0*
Zn, ppm	81 ± 11	422 ± 21	75 ± 10	62 ± 10	62 ± 10	69 ± 10	*14,0*
As, ppm	12 ± 6	18 ± 9	8 ± 6	16 ± 6	14 ± 6	12 ± 6	*50,0*
Rb, ppm	135 ± 10	164 ± 10	113 ± 9	119 ± 9	129 ± 9	134 ± 9	*7,1*
Sr, ppm	305 ± 12	67 ± 7	199 ± 10	321 ± 12	79 ± 8	74 ± 7	*7,2*
Y, ppm	26 ± 9	66 ± 10	35 ± 8	24 ± 9	33 ± 9	35 ± 9	*26,5*
Zr, ppm	162 ± 9	145 ± 8	167 ± 8	161 ± 8	190 ± 8	187 ± 8	*4,9*
Nb, ppm	14 ± 6	16 ± 9	11 ± 6	4 ± 2	5 ± 2	11 ± 5	*47,7*
Pb, ppm	< 10	229 ± 21	20 ± 16	< 10	< 10	< 10	*44,6*
Ba, ppm	602 ± 255	692 ± 209	602 ± 243	360 ± 221	365 ± 171	441 ± 188	*42,5*
Co, ppm	42 ± 19	32 ± 10	12 ± 11	17 ± 7	< 4	< 4	*43,2*
Ag, ppm	32 ± 22	22 ± 9	24 ± 13	17 ± 8	< 4	< 4	*50,6*
Bi, ppm	< 15	53 ± 45	< 15	< 15	41 ± 28	< 15	*76,6*

Summary of non-magnetic results:

- The amount of supper fine particles is highest in clay **E**, **H**, **I** and about two times lower in **D** and **F** clays.

Therefore:

- Clays **E, H** and **I** should contain more clay minerals than **D, F** and **G** clays;

- Strongest magnetic enhancement can be expected for the brownish clays (**E**, **H** and **I**) after experimental firings (having in mind that clay minerals are the main source or iron during heating).

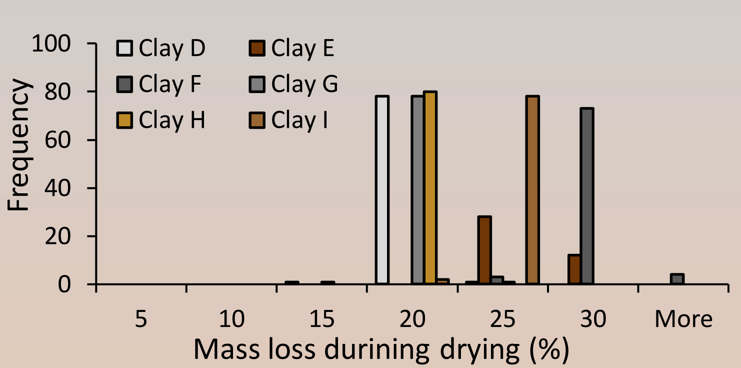
- Typical rock-forming and clay minerals were identified for the studied clays.

- According to their calcium content, the chosen clays can be classified as calcareous (CC) – all grayish clays (**D**, **F**, **G**) possessing calcium content more than 6 % and non-calcareous (NCC) – all brownish clays (**E**, **H** and **I**);

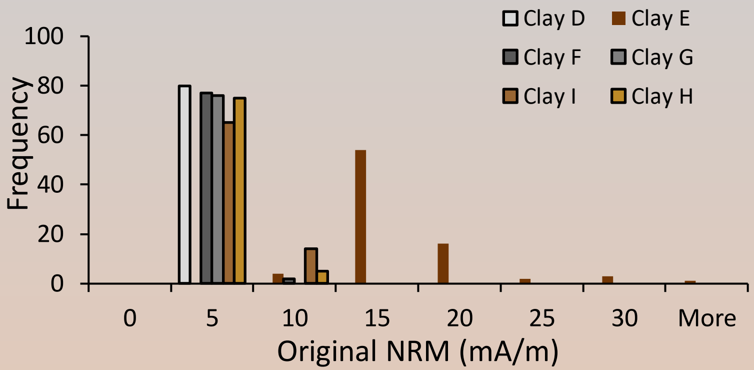
- The most significant mineralogical changes during heating and much more complex mineralogy can be suspected for the calcium-rich **D**, **F**, **G** clays compared to the calcium poor (**E**, **H** and **I**) clays (*e.g. Duminuco et al. 1998; Cultrone et al. 2001; Trindade et al. 2010);*

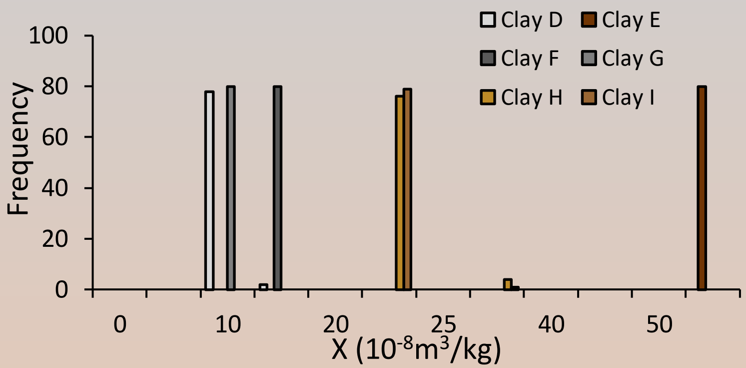
- Montmorillonite is detected in all clays but it appears to be in a relatively higher amount in clays **E, F, H, I** assuming their greater plasticity (especially considering the higher content of superfine clay particles in **E**, **H** and **I** samples) than **D** and **G** clays. This will predeterminate their different water adsorption capability and water loss behavior during heating (*Rice 1987*).

Rock-magnetic properties of raw clays and how they behave during laboratory heating

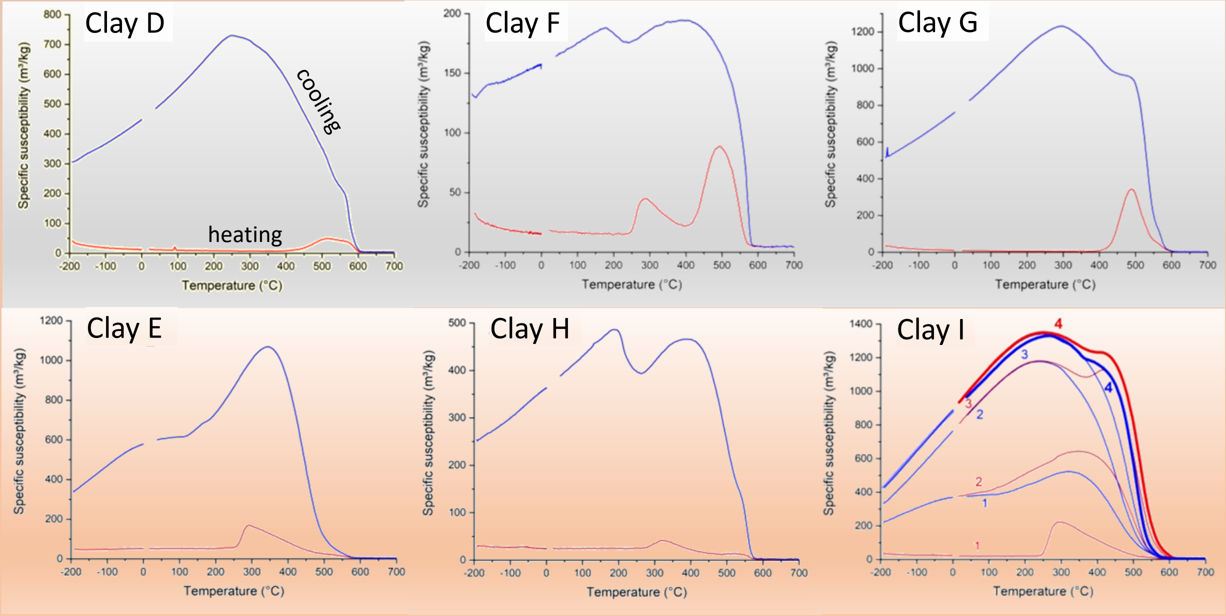


Lighter clays appear to have less adsorption capacity than darker ones, which is likely due to their grain-sizes and mineralogical differences (*Rice 1987*).

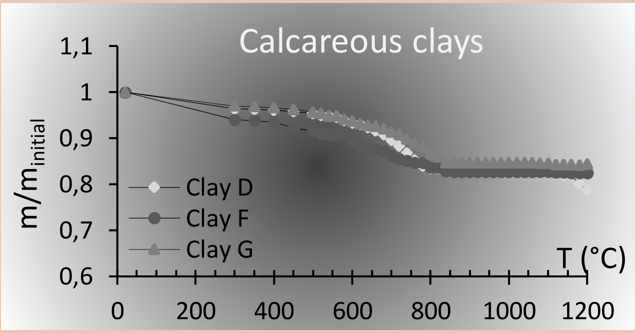


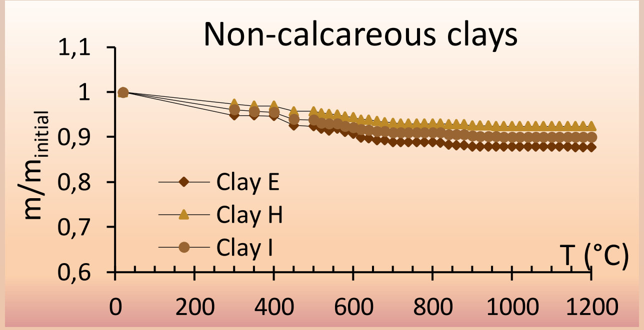


It can be assumed that the brownish clays originally contain more iron oxides than the gray ones.

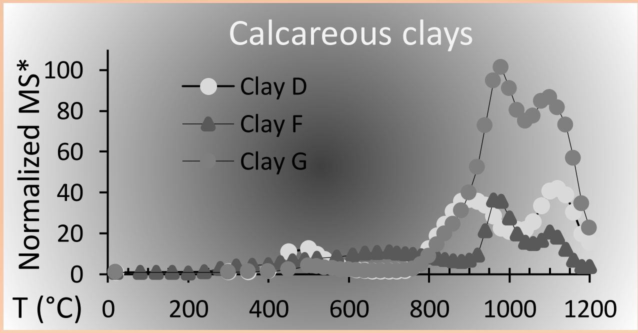


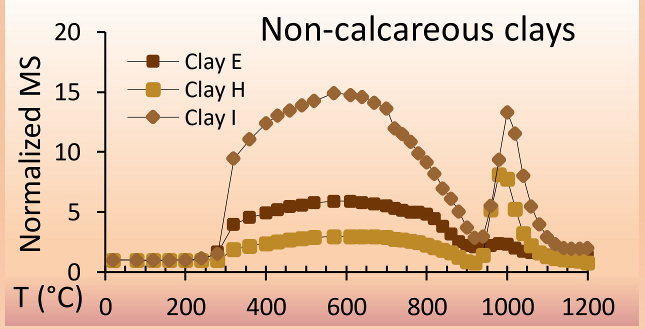
Heating to 700 °C produce a strong magnetic phase in all clays and a single run is not sufficient to complete the mineralogical alterations (see clay **I**).





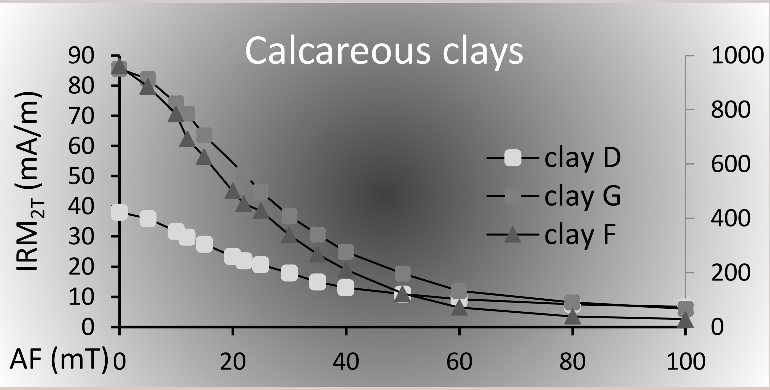
The weight loss trends differ for the CC and NCC. The main lost between 400 – 600 °C for the NCC is likely due to dihydroxylation only, while in the CC, carbonate decomposition and CO_2 degassing may contribute at higher T (*Rice 1987; Bauluz et al. 2003*). The extremely small particles in the finer **E**, **H**, **F**, **I** clays do not allow easily water to escape and the weight decreasing is more gradual.

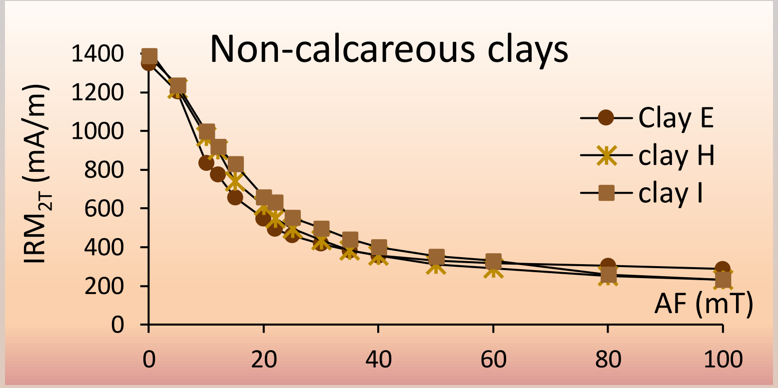


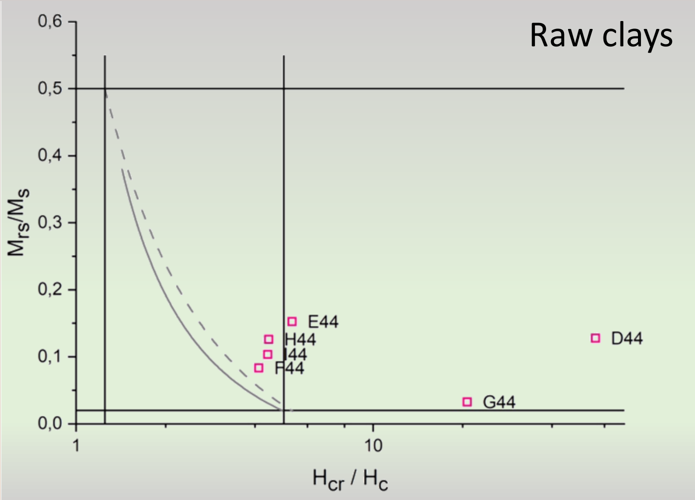


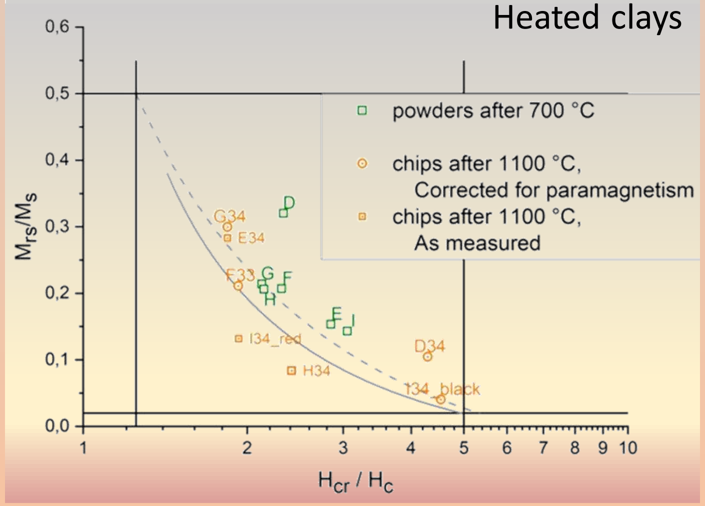
The calcareous clays underwent the strongest mineralogical changes starting at ~ 400 °C and being most pronounced after 800 °C. Non-calcareous clays begin to change earlier (after 280 °C) and there is not much difference in their extent within the whole temperature range.

* *MS – magnetic susceptibility*

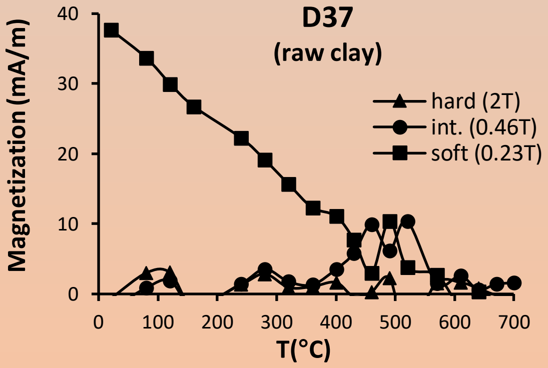


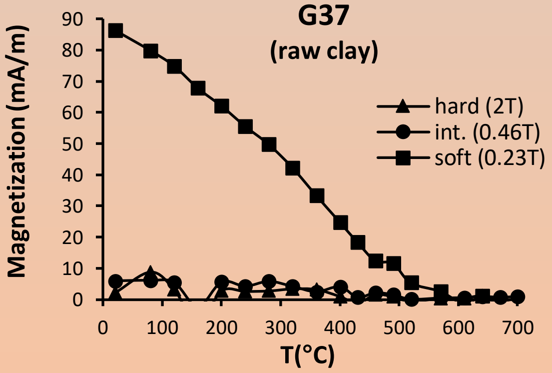


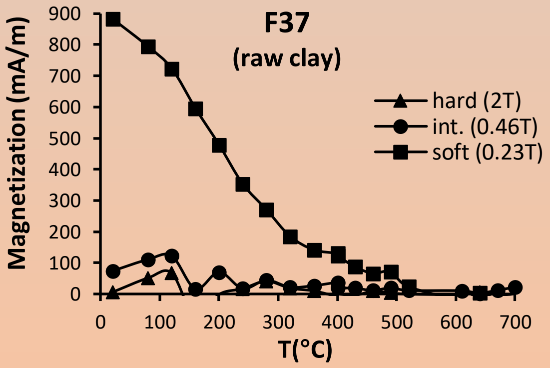


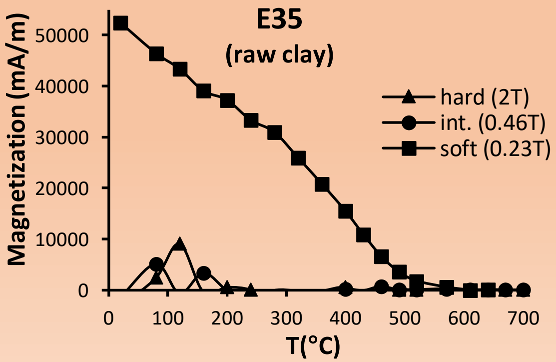


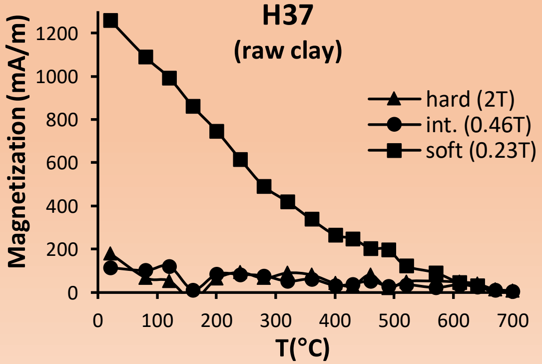
AF demagnetization confirm that CC (especially clay **D**) contain less iron oxides than NCC. Soft magnetic phase prevail in all clays (*AF demag., Lowrie test*) but some amount of high coercivity magnetic mineral (*not detected with Lowrie test*) can be suggested for **D**, **E**, **H** and **I** clays (IRM_{left} after 100 mT exceed 15 %).

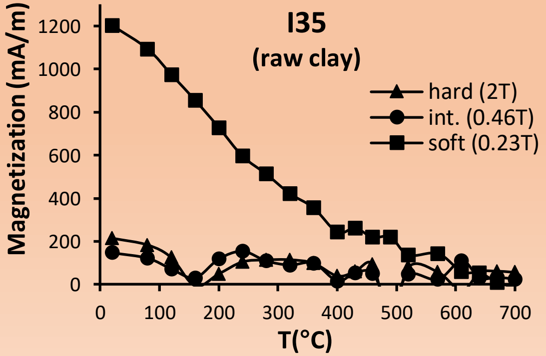








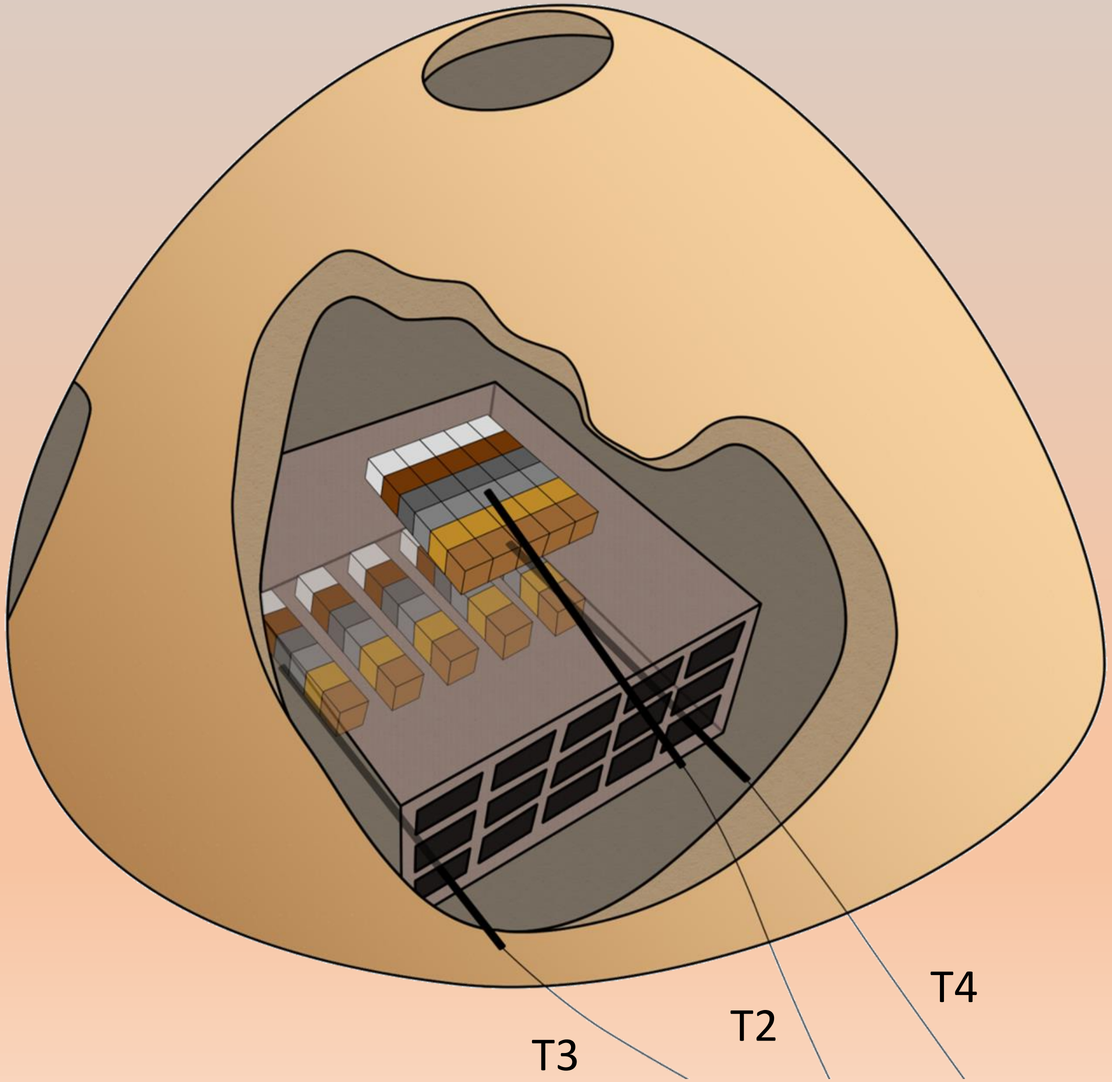




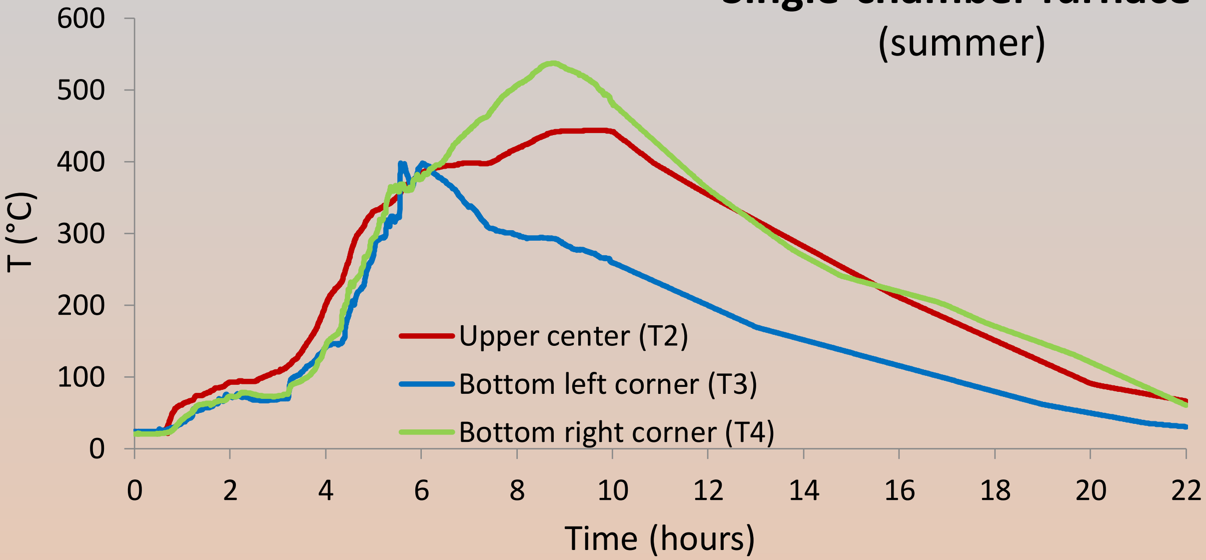
Day plot agree well with the results from the other analysis indicating significant mineralogical difference among clays **D**, **G** and **E**, **H**, **I**. The strongest changes in hysteresis properties are observed for **D** and **G** samples.

Experimental firing

The most prolonged heating/cooling cycle



Single-chamber furnace
(summer)



The temperatures achieved vary between 400 °C (bottom left corner) to 540 °C (bottom right corner) displaying very uneven distribution within the structure after 400 °C.

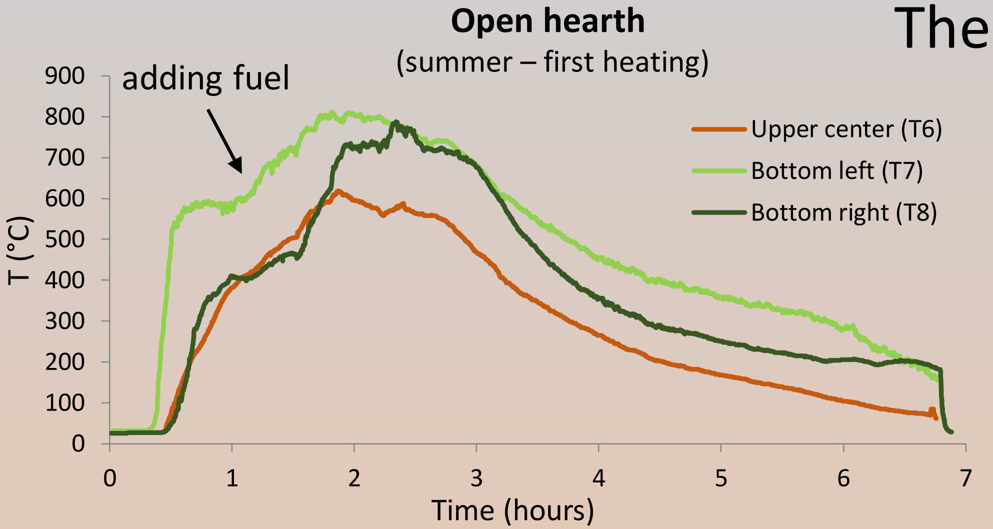
Reaching T_{max} took from 5 h (bottom left corner) to 9 h (bottom right corner) indicating slow heating rate of 1.4 to 0.8 °/min.

Soaking time at 400 °C vary from 6 min (bottom left corner) to almost 5 h (bottom right corner).

Cooling to 200 °C took from ~ 6.5 h (bottom left and right corners) to 8 h (upper center).

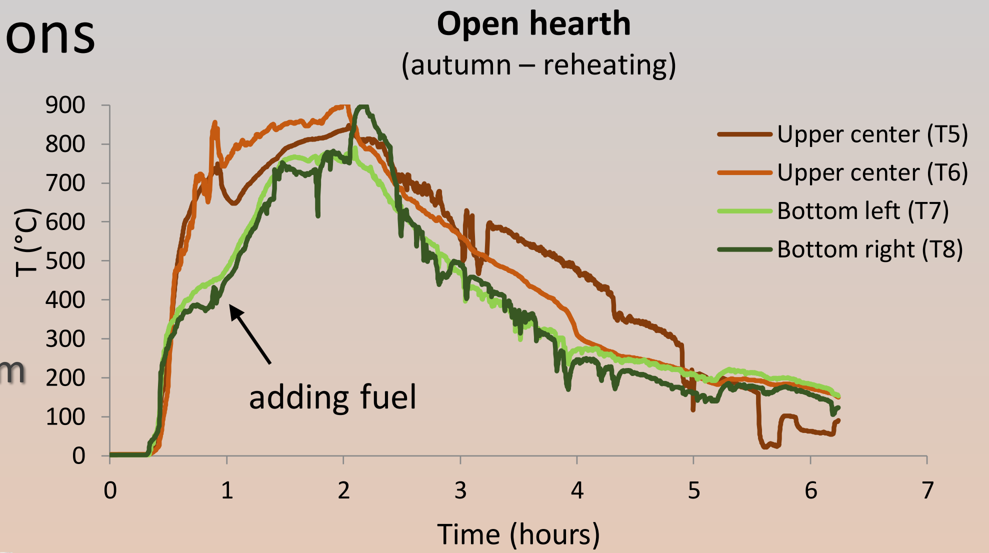
Cooling rate variations (calculated for 10 minutes intervals) are from 1.7 to 0.1 °/min as the highest values correspond to the first hour.

The most variable conditions



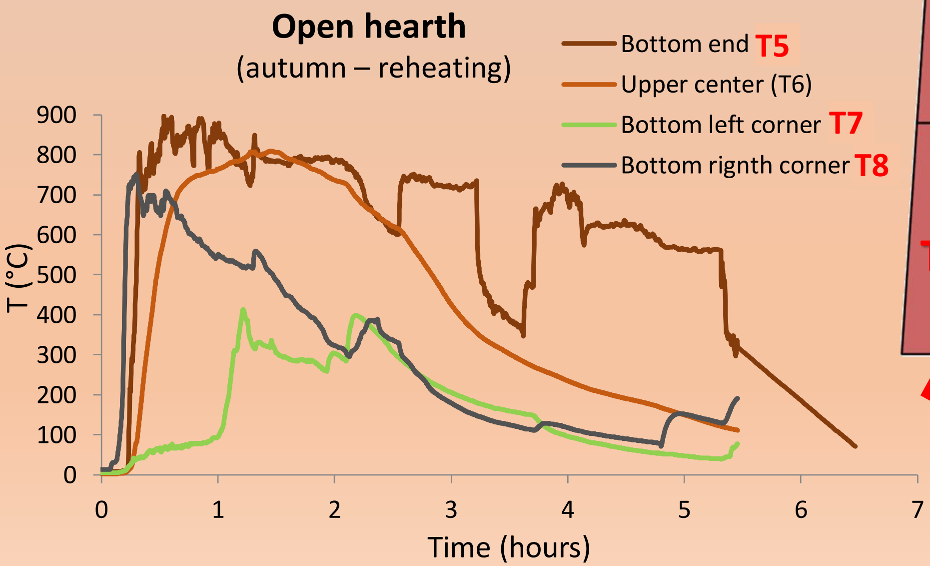
T_{max} was quite different within the fireplace – from 410 °C (bottom-left corner) to 910 °C (upper center).

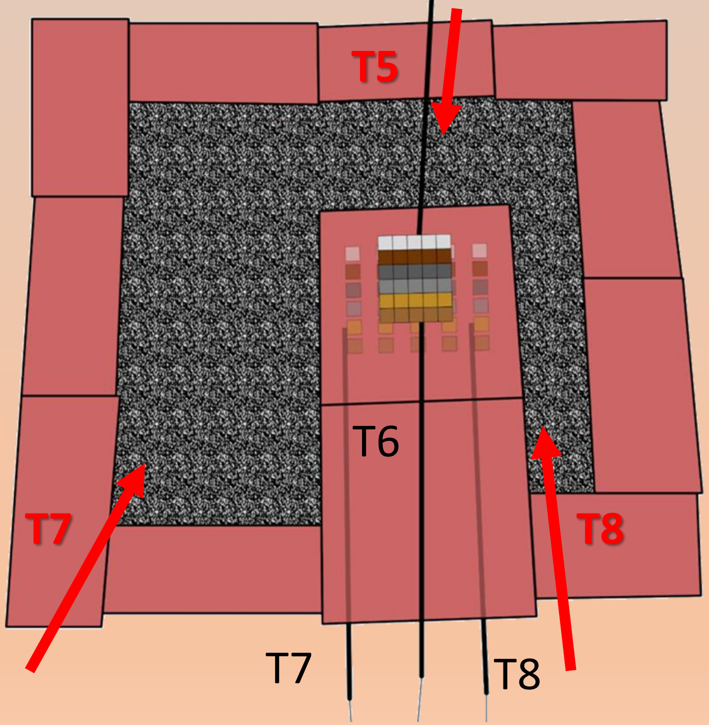
Average heating rates vary from 41 to 4 °/min (no extra fuel).

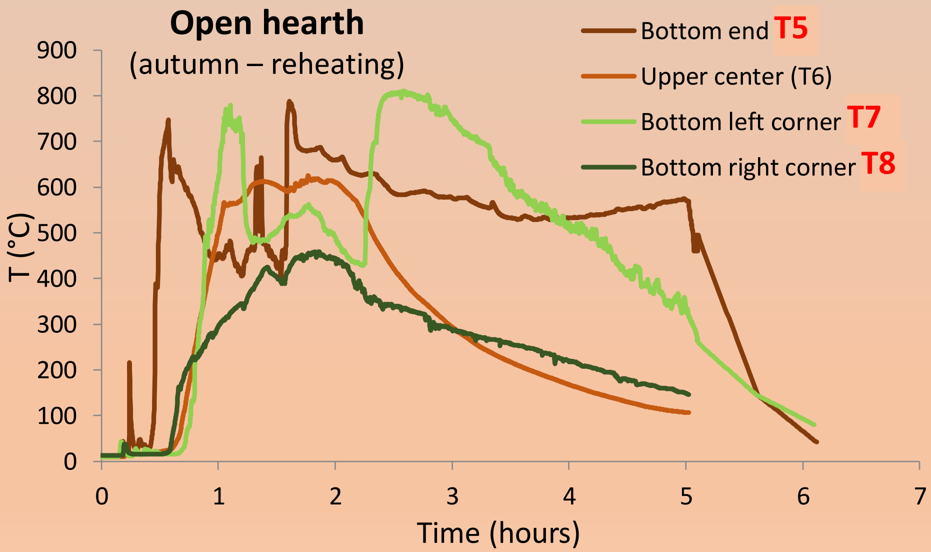


T_{max} were achieved for ~ 2.5 – 3 h (according to the placement of thermocouples) when extra fuel was added and for ~ 18 min – 2.5 h using only the initial fuel.

Soaking time vary from 7 min to almost 3 h at 700 °C and – from 1 min to 1 h at 800 °C.



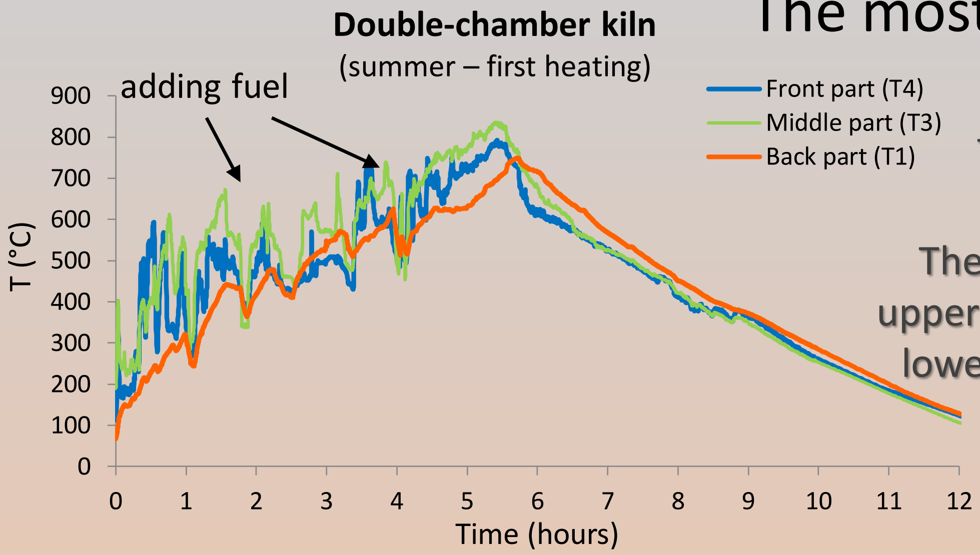




Cooling to 200 °C took from 2.5 h to almost 5 h during the summer, but it is one hour faster during the autumn.

Cooling rate (calculated for 10 min intervals) was quite variable ranging from 18 to 7 °/min within the same cooling process.

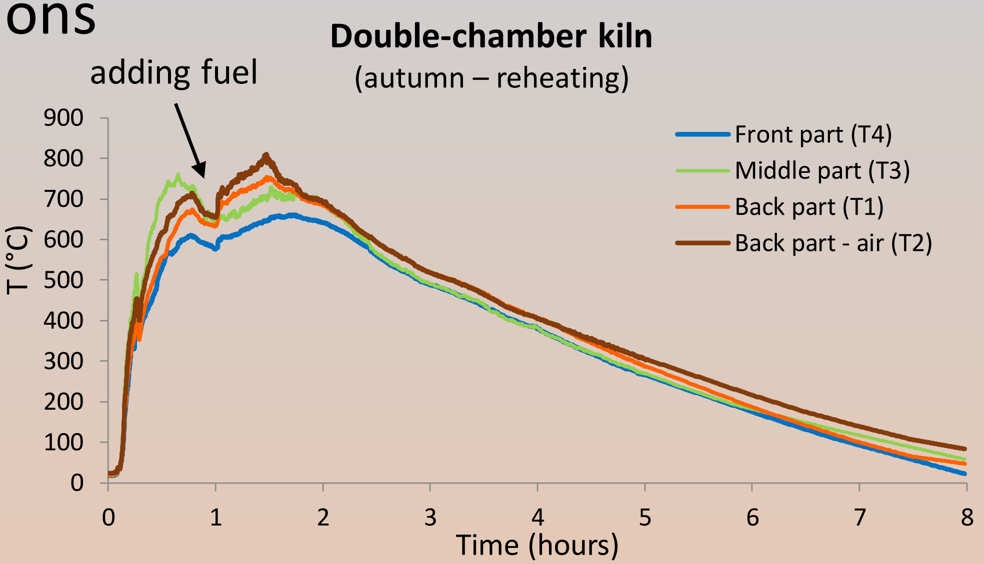
The most homogeneous conditions



T_{max} differ from 145 °C to 7 °C in the different parts of the kiln but it rarely exceed 60 °C.

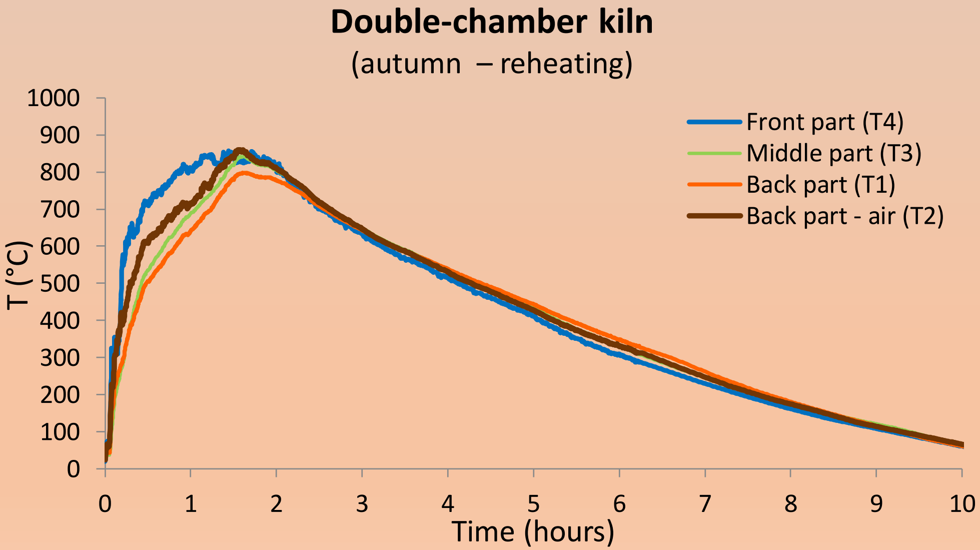
The highest T_{max} correspond to the upper back part of the kiln (T2) and the lowest – to the lower back part (T1).

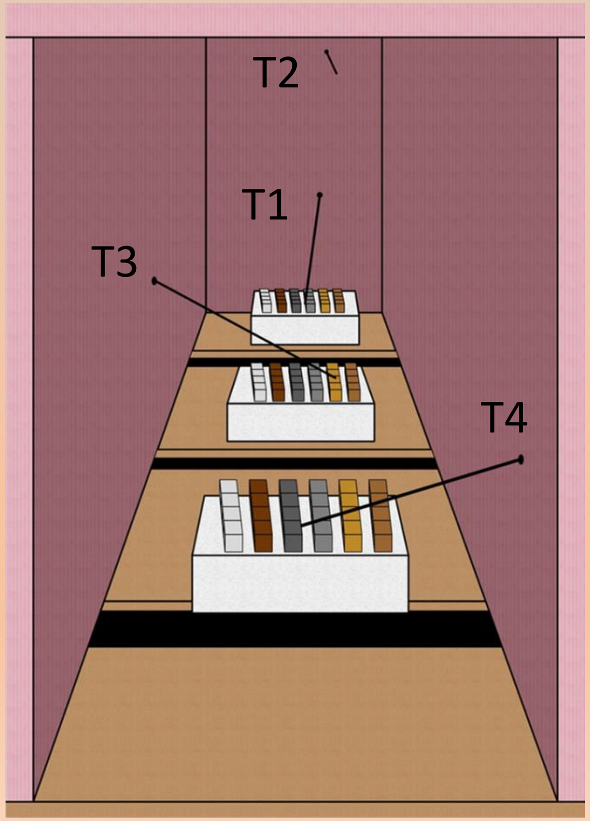
Average heating rates vary from 22 to 5 °/min (no extra fuel).

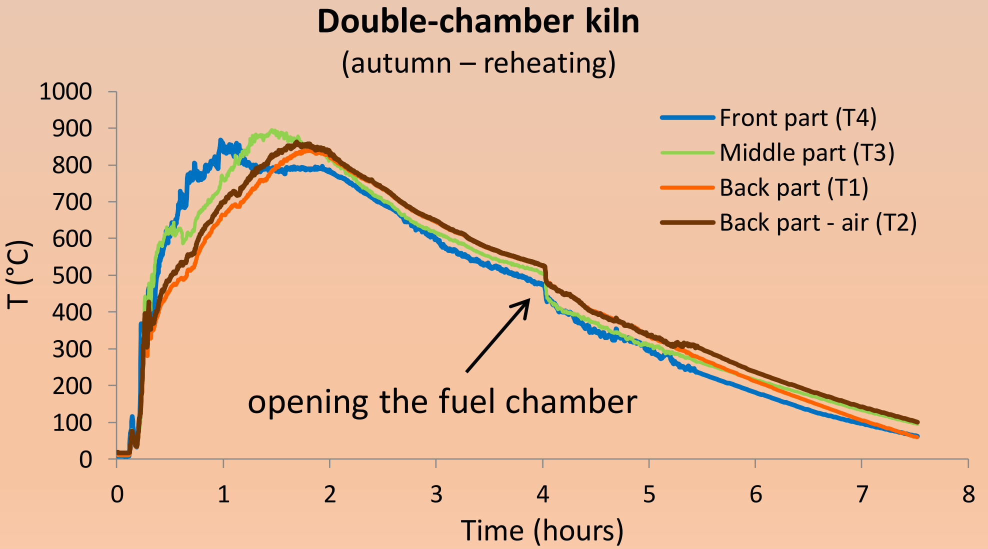


T_{max} were achieved for ~ 0.5 h – 2.5 h according to the placement of thermocouples (no extra fuel).

Soaking time vary from 40 minutes to 2 hours at 700 °C and – from 1 minute to 1 hour at 800 °C.







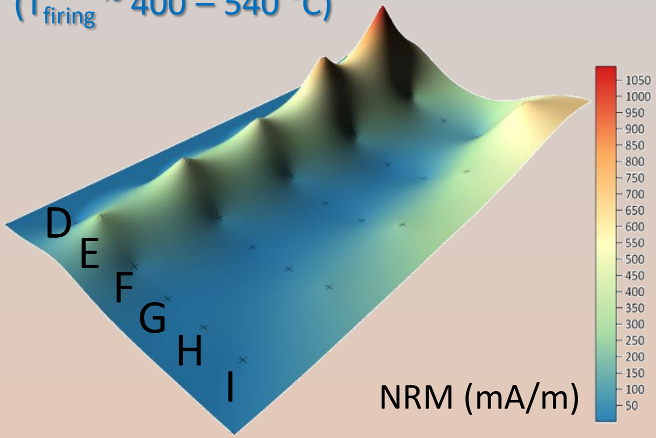
Cooling to 200 °C lasted 4 – 6 h and does not seems affected by the weather. Opening the fuel chamber do not change cooling rate significantly (it took 4-5 h).

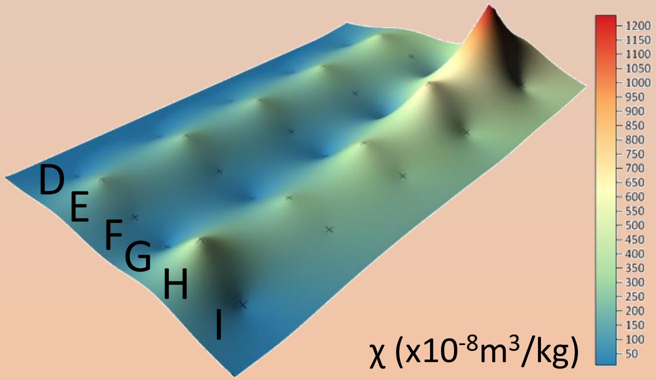
Cooling rate (calculated for 10 minutes intervals) vary from 7 to 2 °/min within the same cooling process being the most variable in the first hour.

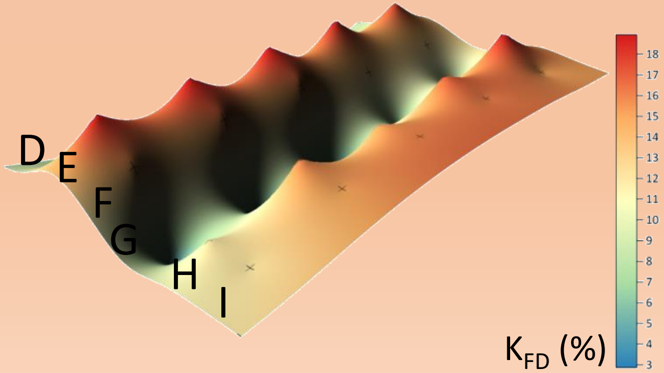
Single-chamber furnace

Bottom part

(T_{firing} ~ 400 – 540 °C)



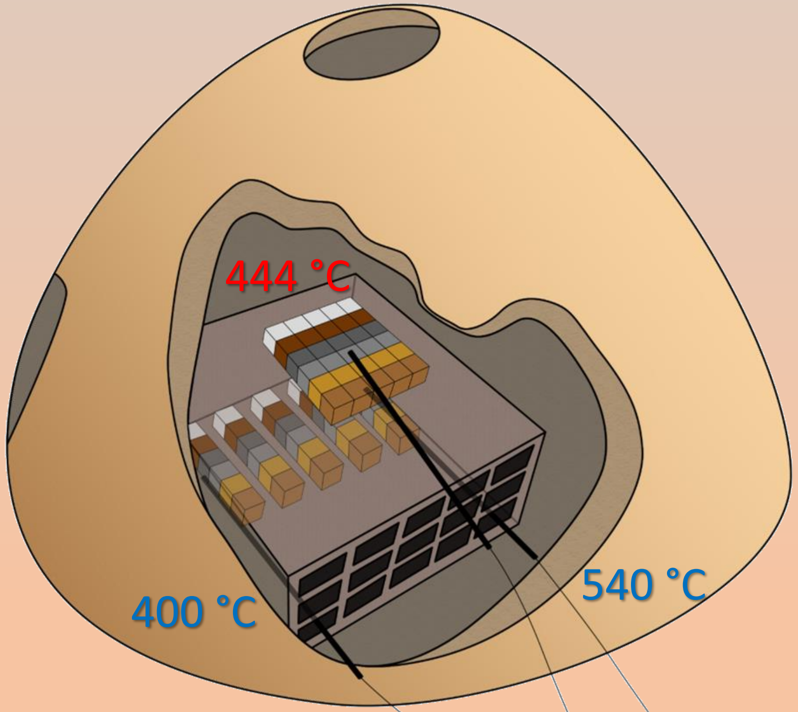




The strongest magnetic enhancement corresponds to the samples in the upper part of the furnace and those closest to the center.

The highest NRM and χ values are registered for **E** and **H** clays and the lowest – for **F** and **G** samples.

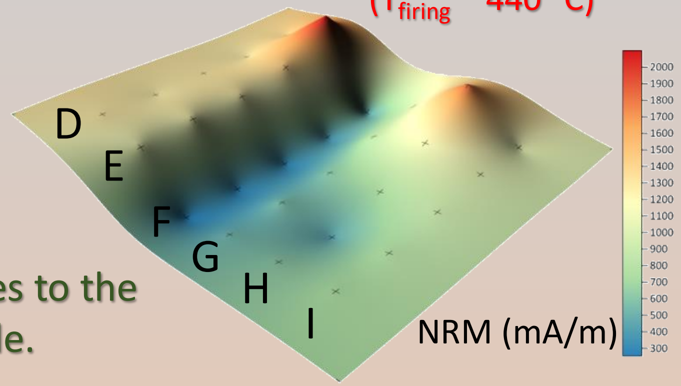
The dependence of NRM and χ values to the sample position is clearly visible.

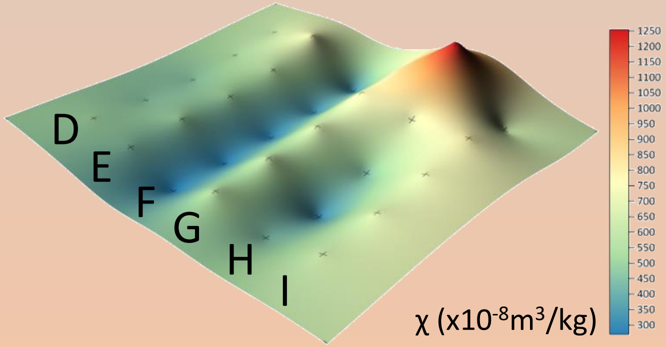


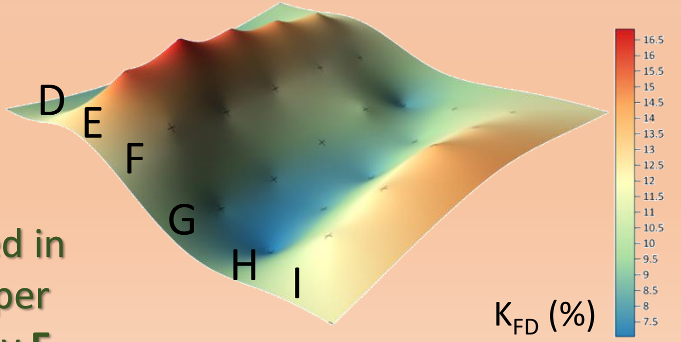
It appears that more SP particles were produced in the bottom part of the furnace than in the upper one. Maximum K_{FD} values are registered for clay **E**, **H**, **I** and minimum – for clay **D** and **G**.

Upper central part

(T_{firing} ~ 440 °C)



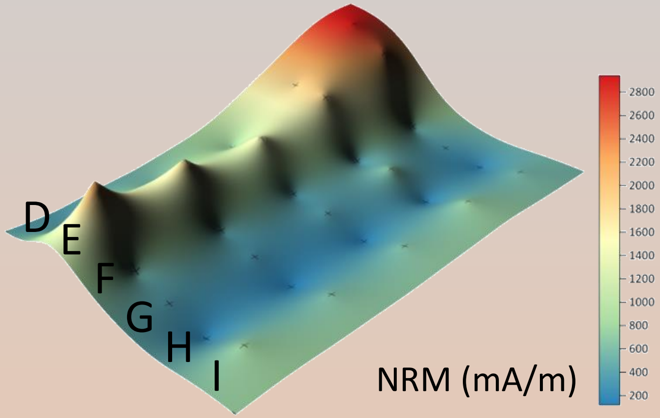


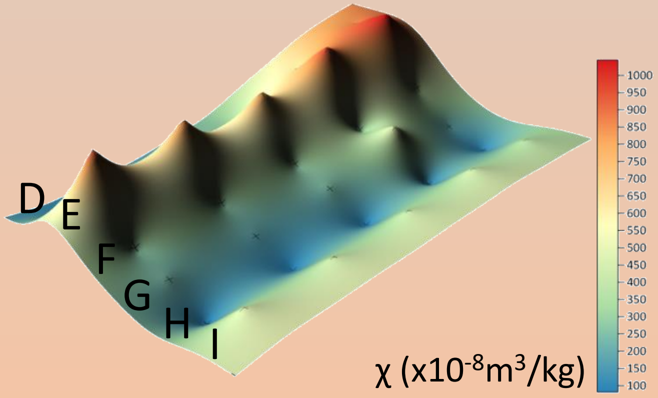


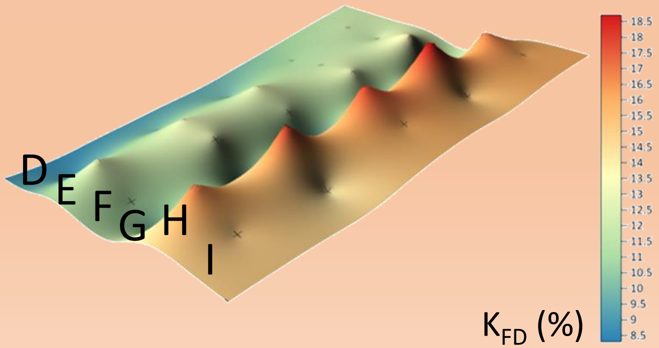
Open hearth – bottom part

Single heating

(T_{firing} ~ 790 – 810 °C)

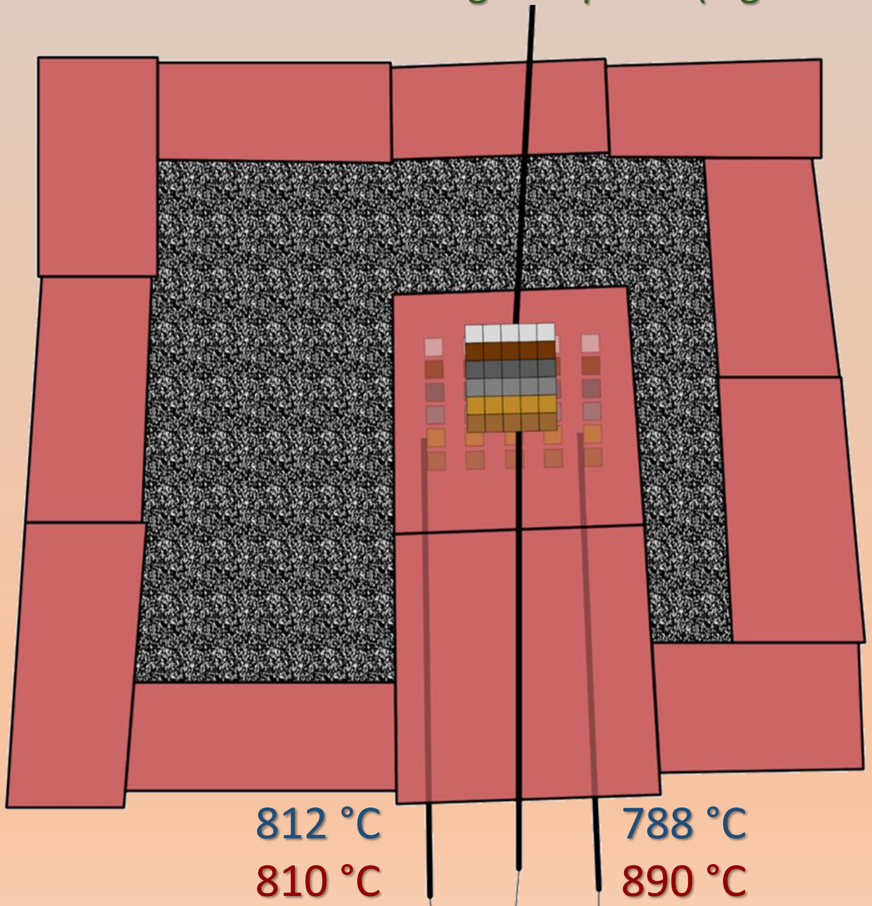






As it was already shown (k-T curves for clay **I**) single heating was not enough to complete the mineralogical changes.

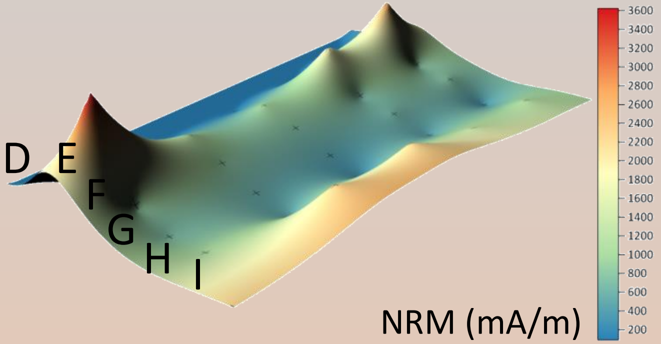
Generally magnetic enhancement increases with the number of firings. Exceptions are clay **D** and some clay **E** samples where lower magnetic signal was measured after reheating likely due to a creation of low magnetic phase (e.g. hematite).

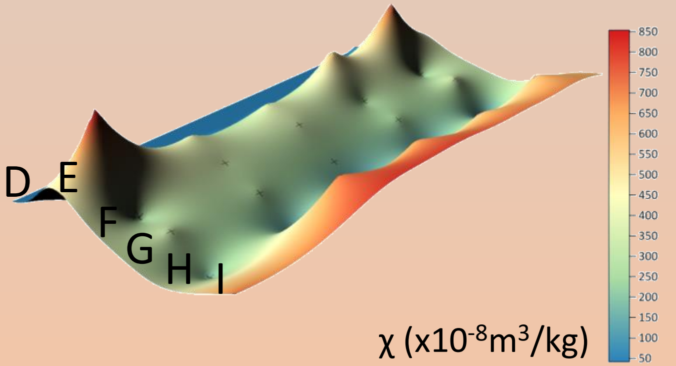


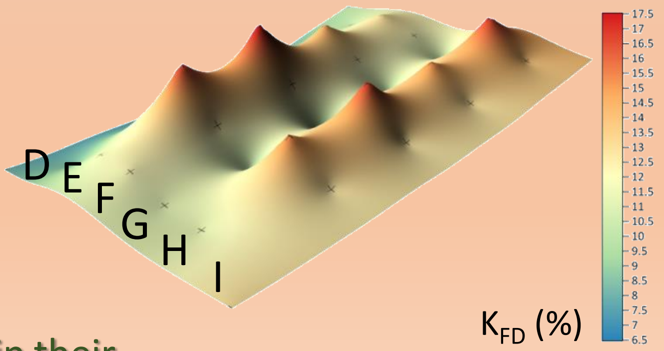
Due to multiple heating more SP particles were produced as again their amount is highest for **E**, **H** and **I** clays and lowest for **D** and **G** samples.

Multiple heating

(T_{firing} ~ 810 – 890 °C)



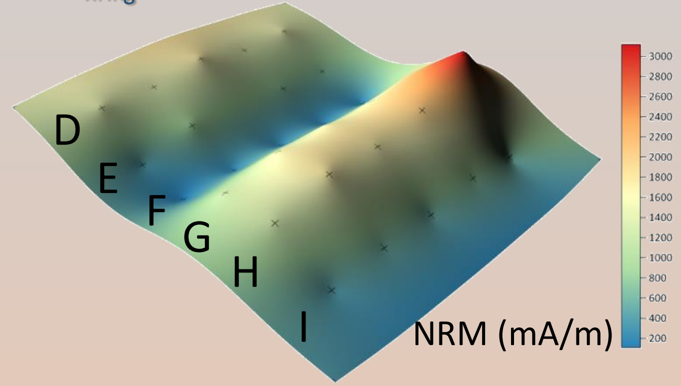


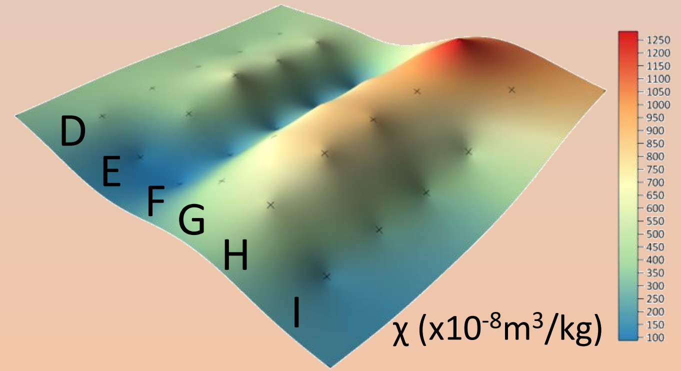


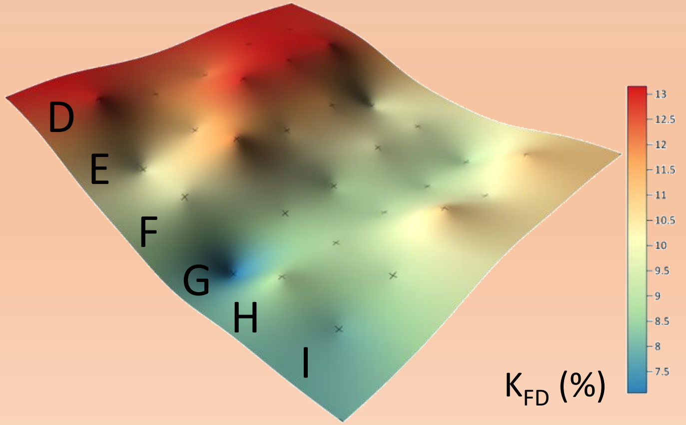
Open hearth – upper part

Single heating

(T_{firing} ~ 620 °C)

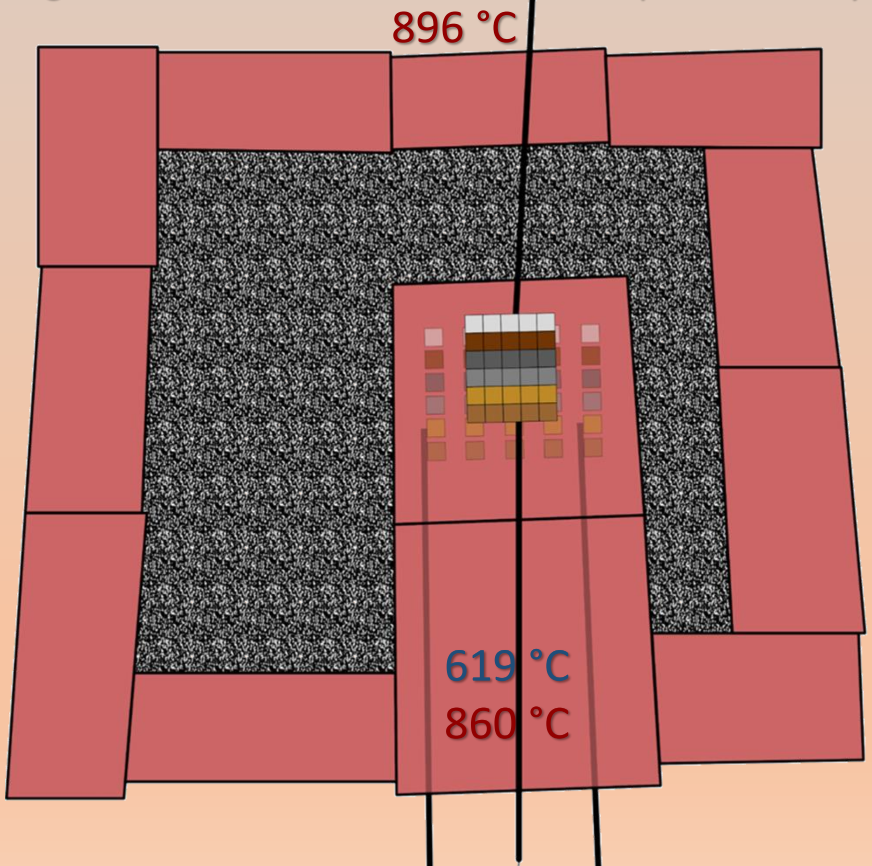






Upper and bottom samples again possess different magnetic properties as the number of firings obviously have different impact.

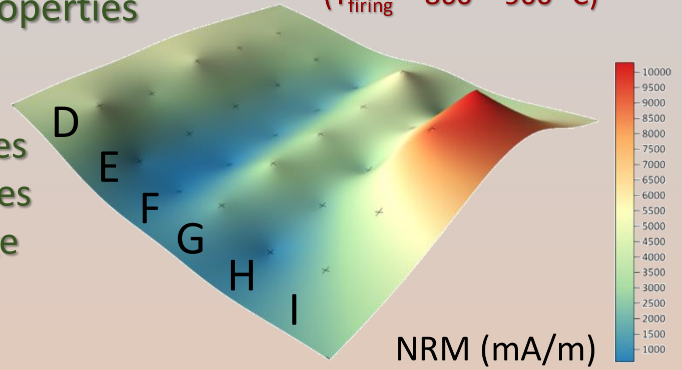
The variability of firing conditions reflect on the magnetic properties and interfere their summarizing. It appear that multiple heating does not reflect on NRM of the upper **D** samples but significantly change their χ values. In contrast to the previous cases the strongest magnetic enhancement does not correspond to **E** clay.

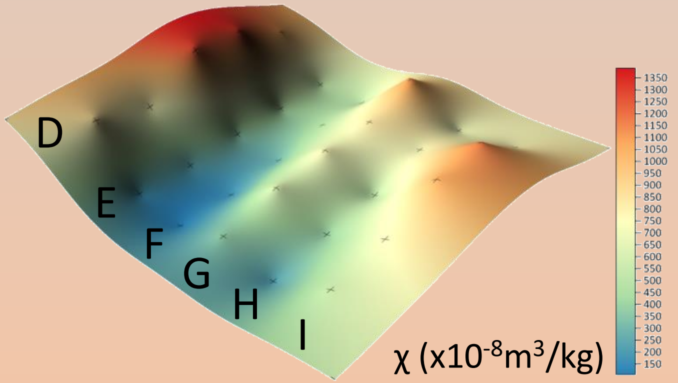


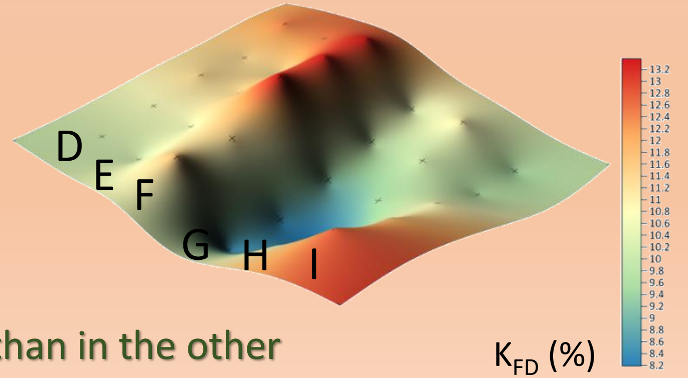
Much more SP particles were produced in **D** and **F** samples than in the other clays and the bottom case but in clay **D** these decrease after reheating.

Multiple heating

(T_{firing} ~ 860 – 900 °C)

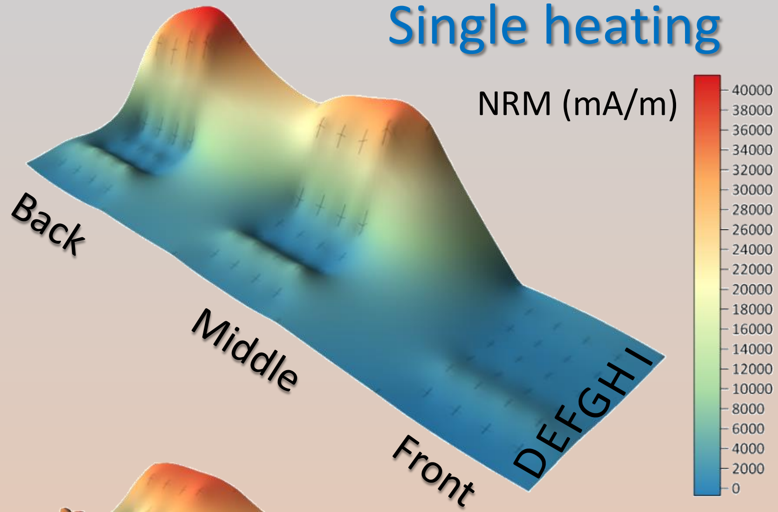


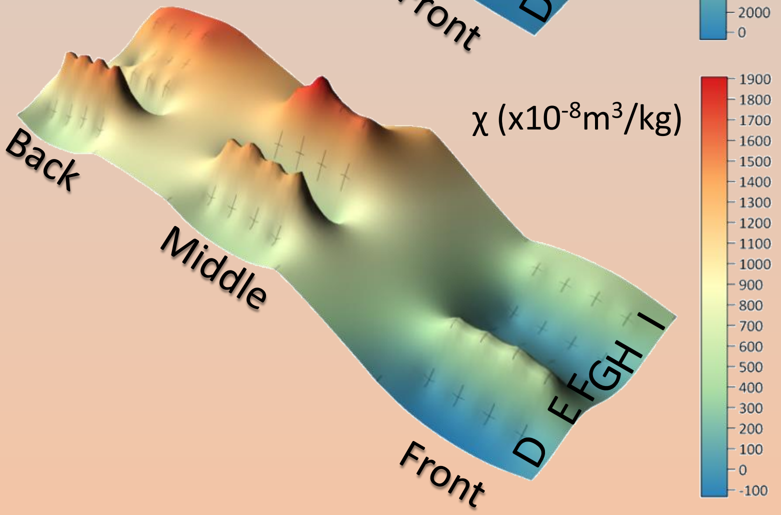


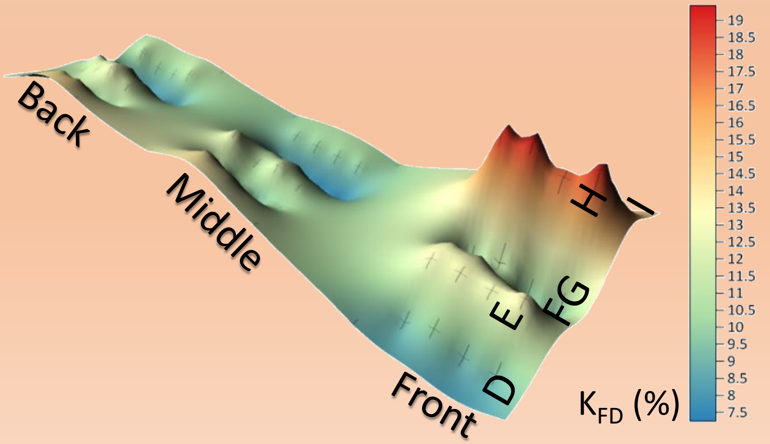


Double-chamber kiln

Single heating

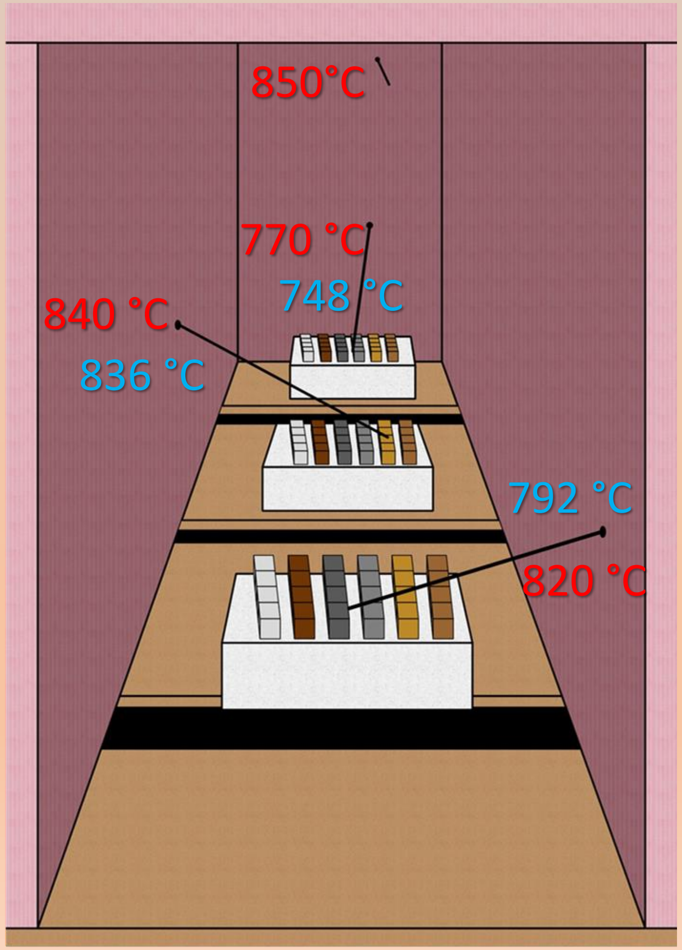




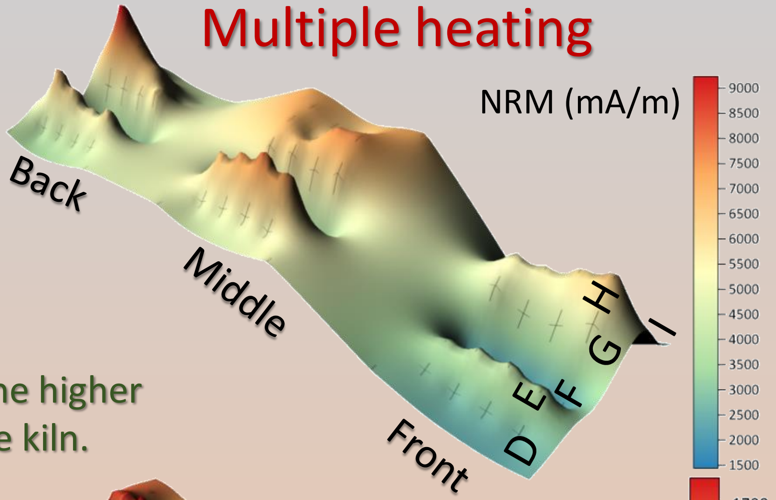


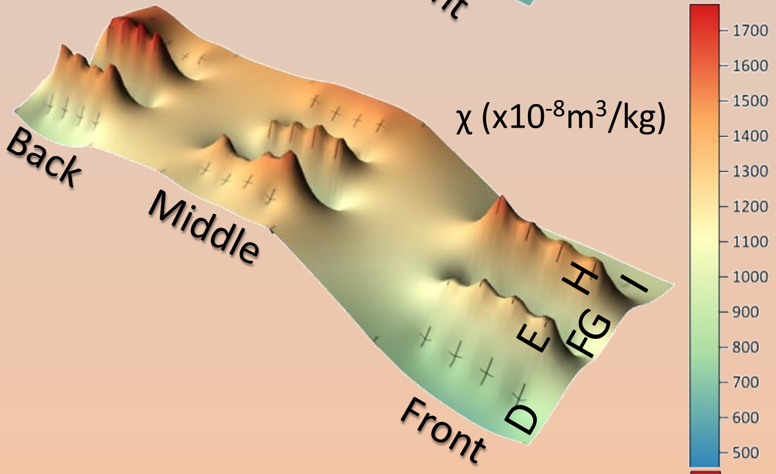
The magnetic properties are much more homogeneous as a result of less variability in the firing conditions. However, there is a noticeable difference among the samples located in the front and middle/back. This can not be explained through T_{max} and soaking time differences.

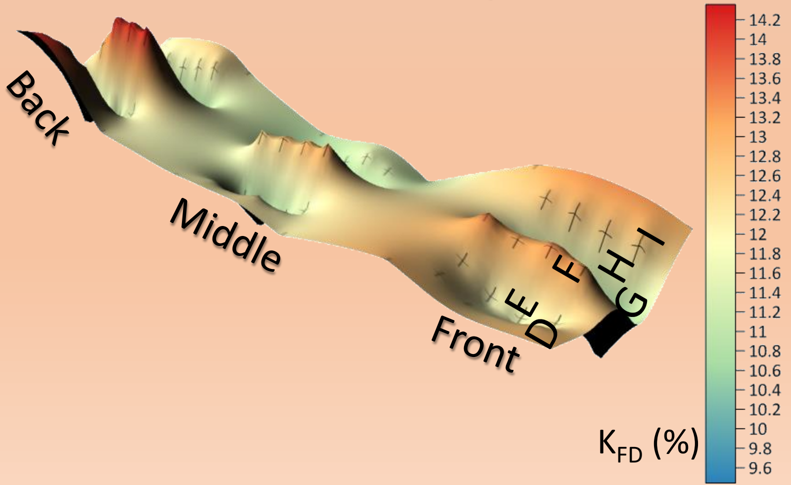
A possible explanation could be the higher oxygen input in the front of the kiln.



Multiple heating







Concluding remarks:

- Non-magnetic analyzes provide valuable information about the studied clays, which contributes to a better understanding of their heating behavior.
- Although, each clay (being composed of different clay minerals and various impurities) behave in a unique way during firing, some similarities among the collected clays are found and two main groups stand out. The first one include all brownish NCC clays (E, **H**, **I**) and the second one is consisted of all CC (**D**, **G** and **F**).
- The strongest magnetic enhancement after experimental firings was observed for the non-calcareous clays (**E**, **H**, **I**). However, calcareous ones (**D**, **G**, **F**) show highest mineralogical changes after 800 °C laboratory heating, which are likely due to the calcite breakdown and formation of new high temperature minerals.
- Single heating at 700 – 800 °C with about one hour soaking time is not enough to complete mineralogical changes in the studied clays.
- The heating/cooling cycle was the most prolonged in the single-chamber furnace and most homogeneous in the double-chamber kilns.
- The variability of firing conditions within the corresponding structure strongly reflect the magnetic properties of the studied clays, which determinates the importance of their placement during their baking.
- Although, relatively homogeneous firing in the double-chamber kiln, the samples heated in the front part have lower magnetic enhancement even after their forth reheating likely due to the higher oxygen supply in this part.
- The accumulated data for parameters of the firing process agree well with these reported from other researchers (*e.g. Maniatis, Tite, 1981; Livingstone Smith 2001; Carrancho, Villalaín 2011; Bințințan, Gligor 2016; Thér et al. 2018; Herve et al. 2019; Francés-Negro 2019; etc.*).
- Additional experiments are planned to be done to get further deeper insight into the type of magnetic behavior and processes involved during heating and especially how they affect the recording of the existing magnetic field.

REFERENCES:

Bauluz, B., Mayayo, M. J., Fernández-Nieto, C., Cultrone, G., González López, M. G. 2003. Assessment of technological properties of calcareous and non-calcareous clays used for the brick-making industry of Zaragoza (Spain). *Applied Clay Science,* 24, 121-126.

Bințințan, A., Gligor, M. 2016. Pottery kiln: A technological approach to Early Eneolithic black-topped production in Transylvania. *Studia Antiqua et Archaeologica,* 22(1), 5-18.

Carrancho, Á., Villalaín, J. J. 2011. Different mechanisms of magnetization recorded in experimental fires: archaeomagnetic implications. *Earth Planet. Sci. Lett.* 312, 176-187.

Cultrone, G., Rodriguez-Navarro, C., Sebastian, E., Cazalla, O., de la Torre, M. J. 2001. Carbonate and silicate phase reactions during ceramic firing. *Eur. J. Mineral.* 2001, 13, 621-634.

Duminuco, P., Messiga, B., Riccardi, M. P. 1998. Firing process of natural clays. Some microtextures and related phase compositions. *Thermochimica Acta,* 321, 185-190.

Francés-Negro, M., Carrancho, A., Pérez-Romero, A., Arsuaga, J. L., Carreter, J. M., Iriarte, E. 2019. Storage or cooking pots? Inferring pottery use through archaeomagnetic assessment of palaeotemperatures. *Journal of Archaeological Science*, 110, 104992.

Hervé, G., Chauvin, A., Lanos, Ph., Rochette, P., Perrin, M., Perron D'arc, M. 2019. Cooling rate effect on thermoremanent magnetization in archaeological baked clays: an experimental study on modern bricks. *Geophysical Journal International,* 217, 1413-1424, https://doi.org/10.1093/gji/ggz076.

Livingstone Smith, A. 2001. Bonfire II: the return of pottery firing temperatures. *Journal of Archaeological Science*, 28, 991-1003.

Maniatis, Y., Tite, M. S. 1981. Technological examination of Neolithic-Bronze Age pottery from central and southeast Europe and from the near east. *Journal of Archaeological Science*, 8, 59-76.

Rice, M. 1987. Pottery analysis: A sourcebook. *University of Chicago Press, Chicago.*

Thér, R., Kallistová, A., Svoboda, Z., Květina, P., Lisá, L., Burgert, P., Bajer, P. 2018. How Was Neolithic Pottery Fired? An Exploration of the Effects of Firing Dynamics on Ceramic Products. *Journal of Archaeological Method and Theory.* https://doi.org/10.1007/s10816-018-9407-x.

Trindade, M. J., Dias, M. I., Coroado, J., Rocha, F. 2010. Firing Tests on Clay-Rich Raw Materials from the Algarve Basin (Southern Portugal): Study of Mineral Transformations with Temperature. *Clays Clay Miner*, 58, 188-204. https://doi.org/10.1346/CCMN.2010.0580205.

ACKNOWLEDGEMENTS

This study is funded by the grant KP-06-N30/2 from the Bulgarian National Science Fund and the grant 19-55-18006 from the Russian Foundation for Basic Research

Thank You
For Your Attention