FIRE IN THE PAST RECORDED IN ARCHAEOLOGICAL REMAINS AND SOILS

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OUTLINE

Part 1. INTRODUCTION to fire effect on the environment

Part 2. THERMAL INFLUENCE on the soil/clay – mechanisms and effects

Part 3. MAJOR IRON (OXY)HYDROXIDES AND CLAY MINERALS – behavior upon heating

Part 4. WILDFIRES AND MAGNETIC EXPRESSION OF FIRE SIGNATURE in natural soils

Part 5. ARCHAEOLOGICAL BURNT CLAY: effects of thermal influence on the magnetic signature

Part 6. MAGNETIC SUSCEPTIBILITY METHOD for evaluation of maximum firing temperature of archaeological pottery fragments – methodology, advantages and drawbacks

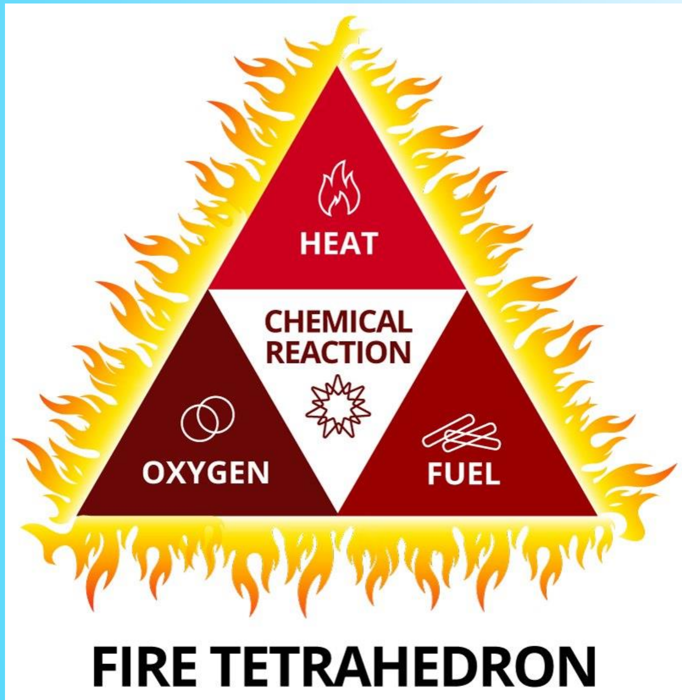
PART 1

INTRODUCTION
to fire effects on the environment

WHAT IS FIRE

Fire: exothermic chemical process of combustion involving the oxidation of a fuel source at a high temperature. During the combustion energy is released and produces heat and light.

4 elements must be present for the fire to exists:

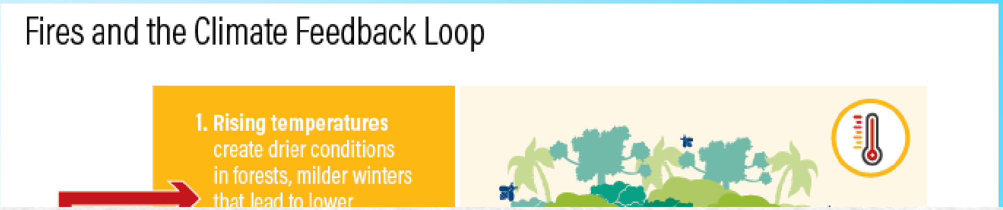


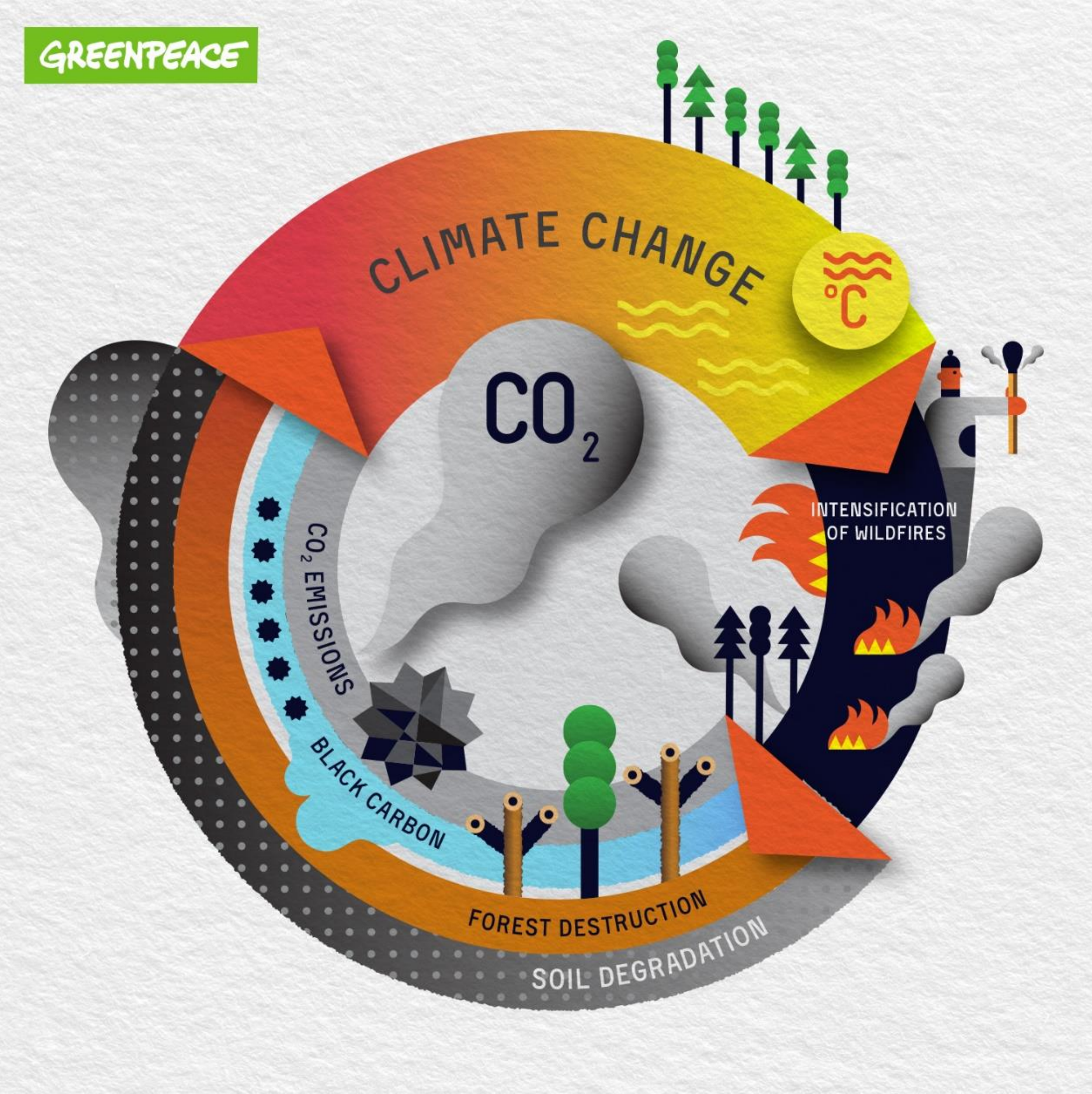
- **Fuels** can be solids, liquids or gases. During the chemical reaction that produces fire, fuel is heated to such an extent that it releases gases from its surface.

- Gases are made up of molecules. When these gases are hot enough, the molecules in them break apart and fragments of molecules rejoin with oxygen from the air to make new product molecules – water molecules (H_2O) and carbon dioxide molecules (CO_2) – and other products if burning is not complete

- If there is not enough oxygen available during a chemical reaction, incomplete combustion occurs, and products such as carbon (C) and carbon monoxide (CO), plus water and carbon dioxide are produced. Less heat energy is released during incomplete combustion than complete combustion.

FIRE EFFECTS ON THE ENVIRONMENT





Fire is recognized as a global phenomenon

More than 30% of the land surface is subjected to a significant frequency of fires

Wildfires play important role in shaping Earth's climate

WILDFIRE characteristics

The intrinsic characteristic of fire is heat that is released during the process of combustion

Fire intensity related to soil properties is defined as the maximum temperature recorded at a certain point and the time that this temperature persists, expressed in °C/s (Úbeda,1998)

Ash (the residue produced by wildfire) can be used as an indicator of fire severity since it is the product of the combustion of biomass.

The color of ash produced under laboratory conditions can be compared with the ashes generated in wildfires to estimate fire intensity.

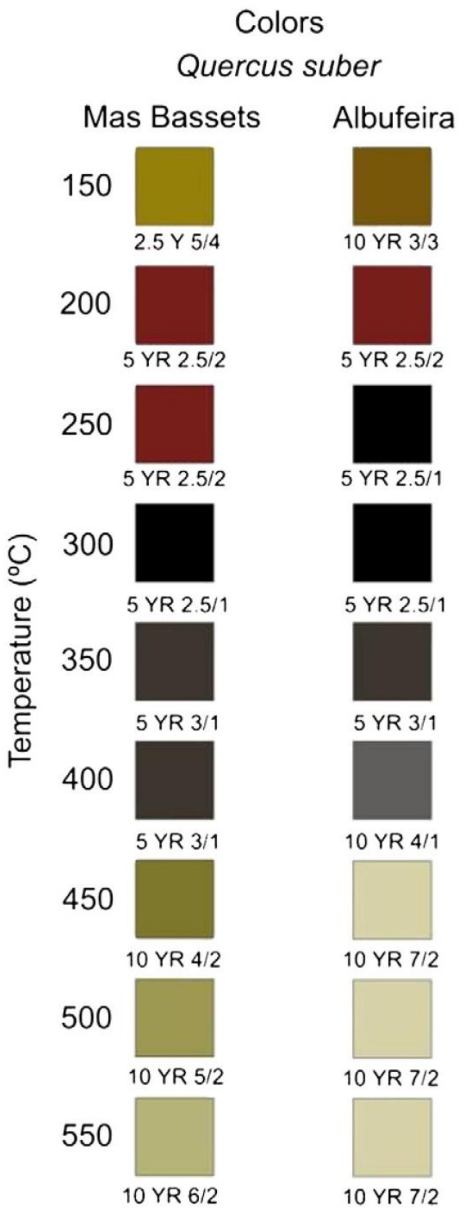
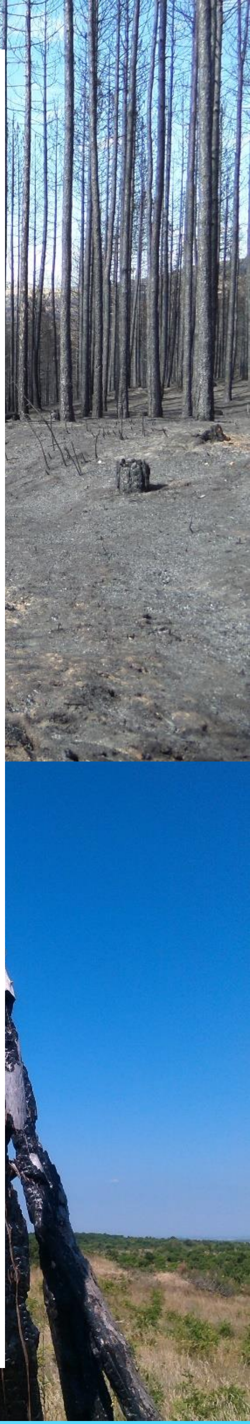


Fig. 1. Example of different ash colors produced under laboratory conditions using leaf litter from two locations (Spain and Portugal) with cork oak (*Quercus suber*) forest (Úbeda et al., 2009).



FIRE EFFECTS ON SOIL PROPERTIES

Regulating factors:
Weather, landscape, land use

Immediate fire effects

- Direct heating
- Volatilization Ash convection
- Deposition of ash and altered fuels
- Exposure of mineral soil

Post-fire, emergent effects

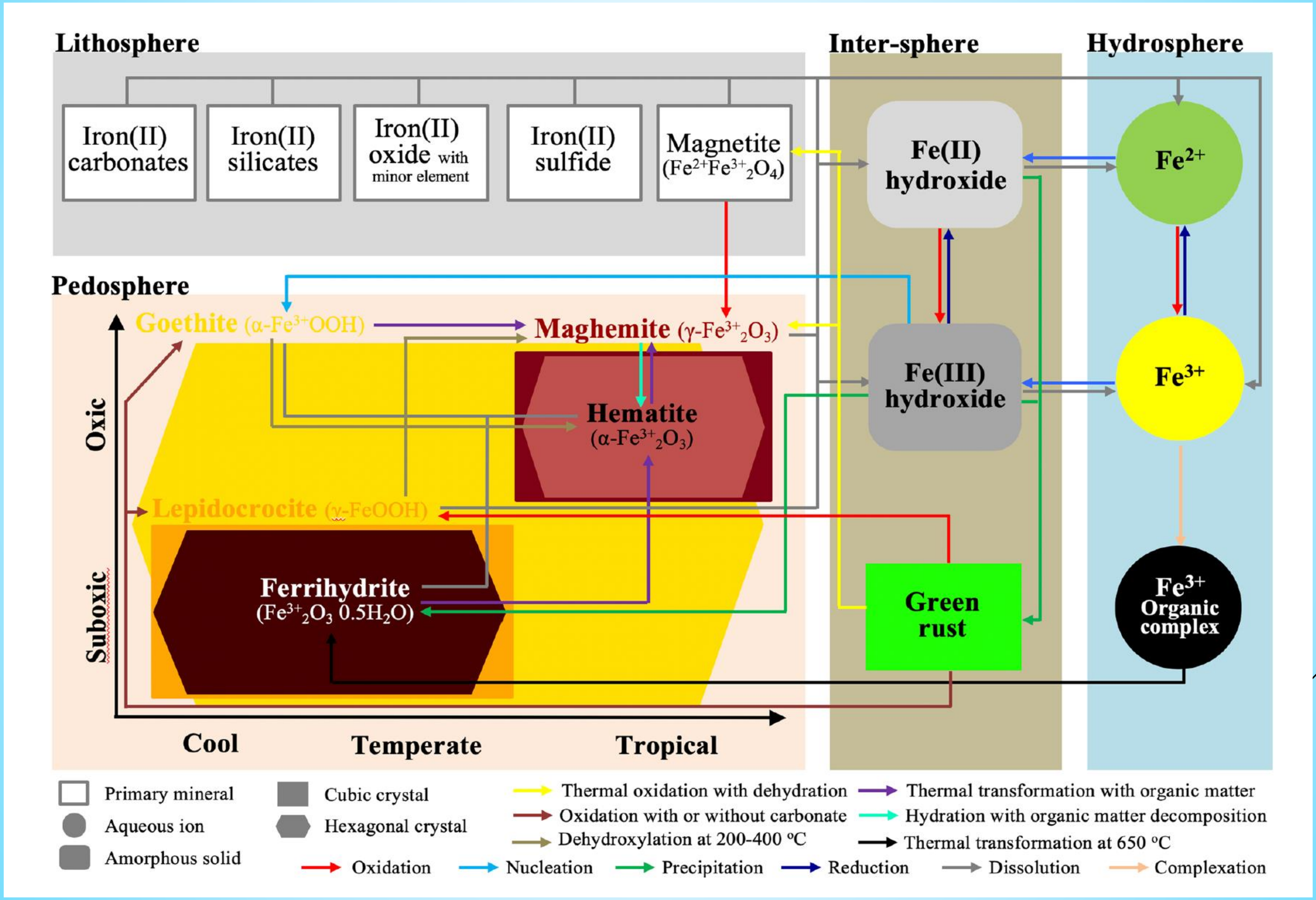
- Hydrophobicity erosion
- Microclimate alteration
- Leaching of nutrients
- Variation in nutrient availability
- Recolonization by soil organisms

Source: *Boerner, Ralph E.J. 2006. Soil, fire, water, and wind: how the elements conspire in the forest context. In: Dickinson, Matthew B., ed. 2006. Fire in eastern oak forests: delivering science to land managers, proceedings of a conference; 2005 November 15-17; Columbus, OH. Gen. Tech. Rep. NRS-P-1. Newtown Square, PA: U.S. Department of Agriculture, Forest Service, Northern Research Station: 104-12*

PART 2

THERMAL INFLUENCE on the soil/clay – mechanisms and effects

IRON (HYDR)OXIDES AND THE COMMON PATHWAYS OF FORMATION AND TRANSFORMATION IN THE ENVIRONMENT

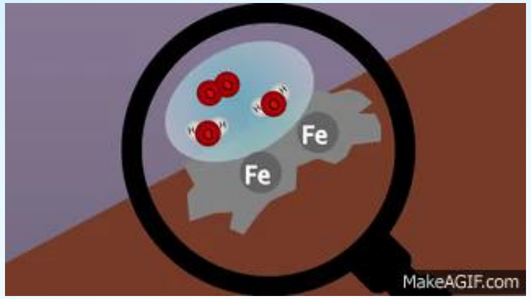


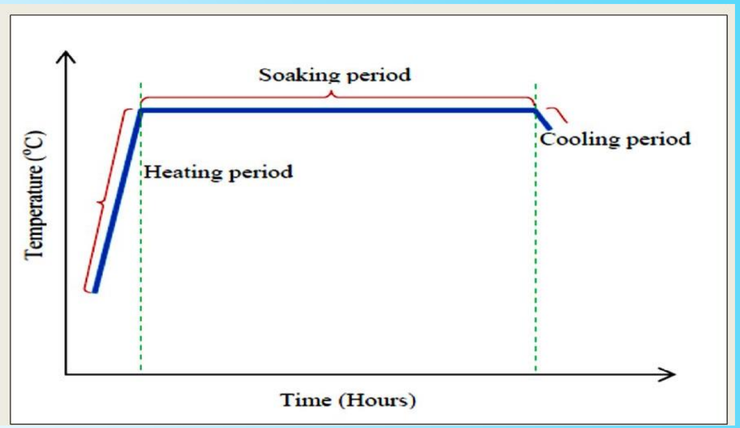
Source: Han et al., 2020, Environmental Chemistry Letters (2020) 18:631–662

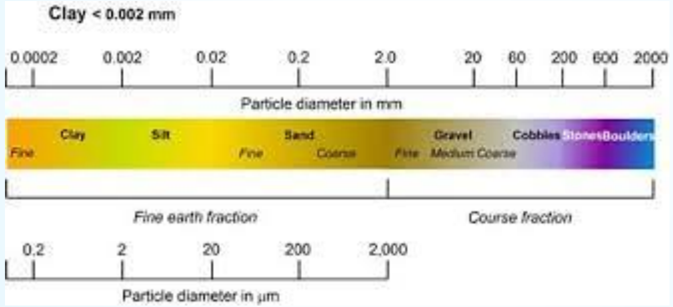
IRON (OXY)HYDROXIDES HIGH TEMPERATURE TRANSFORMATIONS

Transformation path depends on:

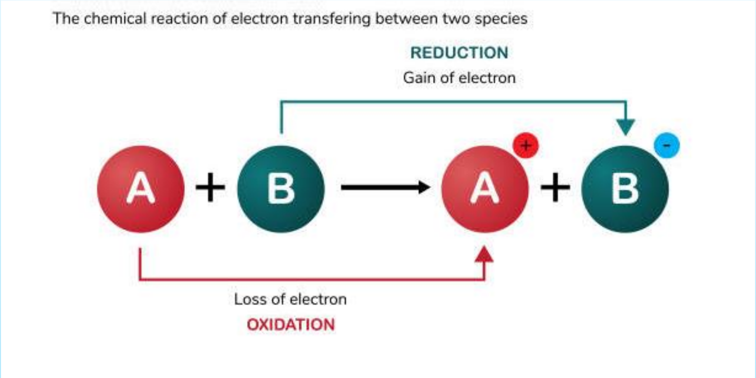
- atmosphere (oxidizing vs reducing)
- particle size
- heating rate
- annealing/soaking time







The most prominent Fe-(oxy)hydroxides property is the changing redox state



PART 3

MAJOR IRON (OXY)HYDROXIDES AND CLAY MINERALS
– behavior upon heating

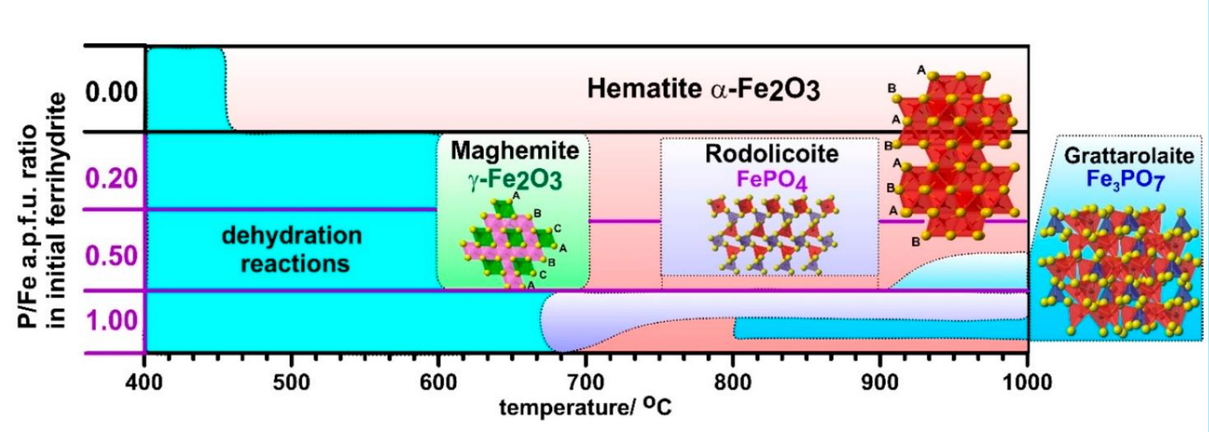
HIGH TEMPERATURE TRANSFORMATION PATHWAYS OF MOST COMMON FE-(OXY)HYDOXIDES

Ferrihydrite $Fe_5OH_8.4H_2O$

No C source	T (°C)		323	370	399	▲ 430	449		700		999
	Phases		—Fh, Hm?—		— Fh, Hm —		—		Hm		—
1% glucose	T (°C)	301	325▲	372				503			
	a (nm)	0.8320 (1)	0.8343 (5)	0.8348 (4)				0.8357 (4)			
	Phases	Fh, Mh, Hm	—	Mh/Mt, Hm				—			
2% glucose	T (°C)	291▲	329					504			
	a (nm)	0.8358 (5)	0.8355 (5)					0.8360 (7)			
	Phases	Fh, Mh/Mt, Hm	—	Mh/Mt, Hm				—			
5% glucose	T (°C)	▲		372				501			
	a (nm)			0.8369 (6)				0.8364 (7)			
	Phases			—	Mh/Mt			—			
10% glucose	T (°C)	283	▲	373				505		999	1000*
	a (nm)	0.8360 (2)		0.8372 (7)				0.8367 (7)		0.8393 (6)	0.8394 (6)
	Phases	Fh, Mh/Mt, Hm?		— Mh/Mt —				— Mh/Mt, Hm? —		— Mt, Hm, Wt —	
20% glucose	T (°C)			▲ 376							999
	a (nm)			0.8379 (7)							0.8401 (8)
	Phases			— Fh, Mh/Mt —							– Mt, Hm, Wt –

Fh = ferrihydrite, Hm = hematite, Mh = maghemite, Mt = magnetite, Wt = wüstite.
? indicates that identification of the phase is uncertain.
▲ indicates the approximate temperature of a DTA exothermic peak maximum.
* indicates that the top 2 mm of sample (not shown) differed from the remainder, which is shown in the table.
Numbers enclosed in brackets indicate the number of lines used to calculate unit-cell edge lengths.

Source: Campbell et al., 1997, Clay Minerals (1997) 32, 615-622



Schematic presentation of temperature ranges of phase stability during ther
transformations of P-doped ferrihydrite (source: Pieczara et al., 2020, Materi

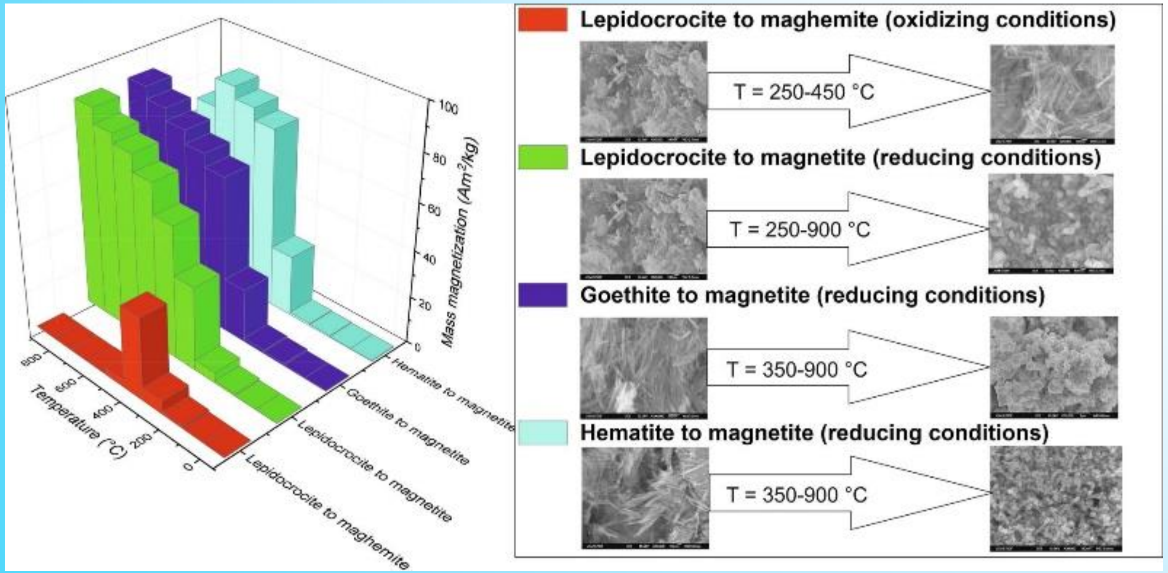
Goethite α-FeOOH

in air: α-FeOOH → T° (155°C - 610°C) dehydroxilation → α-Fe_2O_3 + H_2O

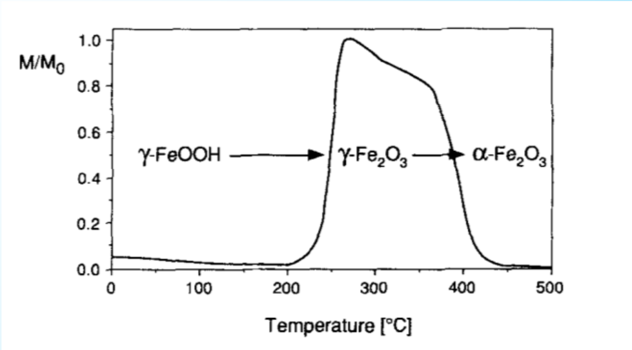
reduction (presence of organic matter): 72 α-FeOOH + $C_6(H_2O)_5$ → T° (650°C - 700°C) reduction → 24 Fe_3O_4 +6 CO_2+ 41 H_2O

lepidocrocite γ-FeOOH

γ-FeOOH → T° (230°C - 400°C) dehydroxilation → γ-Fe_2O_3 → α-Fe_2O_3



Source: *Ponomar et al., 2020, Advanced Powder Technology, 31, 2587-2596*



Gehring and Hofmeister, Clays and Clay Minerals 42, (4), 409-415, 1994.

maghemite γ-Fe_2O_3

thermally unstable mineral

grain-size dependent behavior upon heating:

crystalline well developed particles

~ 300-400°C grain-size dependent

higher transition T due to doping ions

α-Fe_2O_3

coarser grains than initial mht

Machala et al., 2011, Chem. Mater. 2011, 23, 3255–3272

nanoparticles (30 – 80 nm) (superparamagnetic)

500 – 750 °C depending on grain size

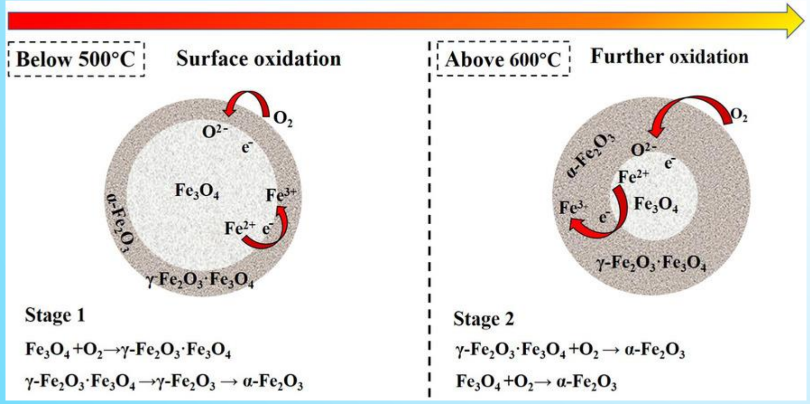
ε-Fe_2O_3 → α-Fe_2O_3

ε-Fe_2O_3

intermediate polymorph to hematite
giant coercive field (Bc) of ~2 T
Ms ≈ 15−25 Am2/kg
Tucek et al., Chem. Mater. 2010, 22, 24, 6483–6505

magnetite Fe_3O_4

oxidation in air



Source: Zhang et al., 2021, steel research int. 2021, 92, 2000687

reduction (H_2/N_2 gas)

micro-sized Mgt (200-350 nm)

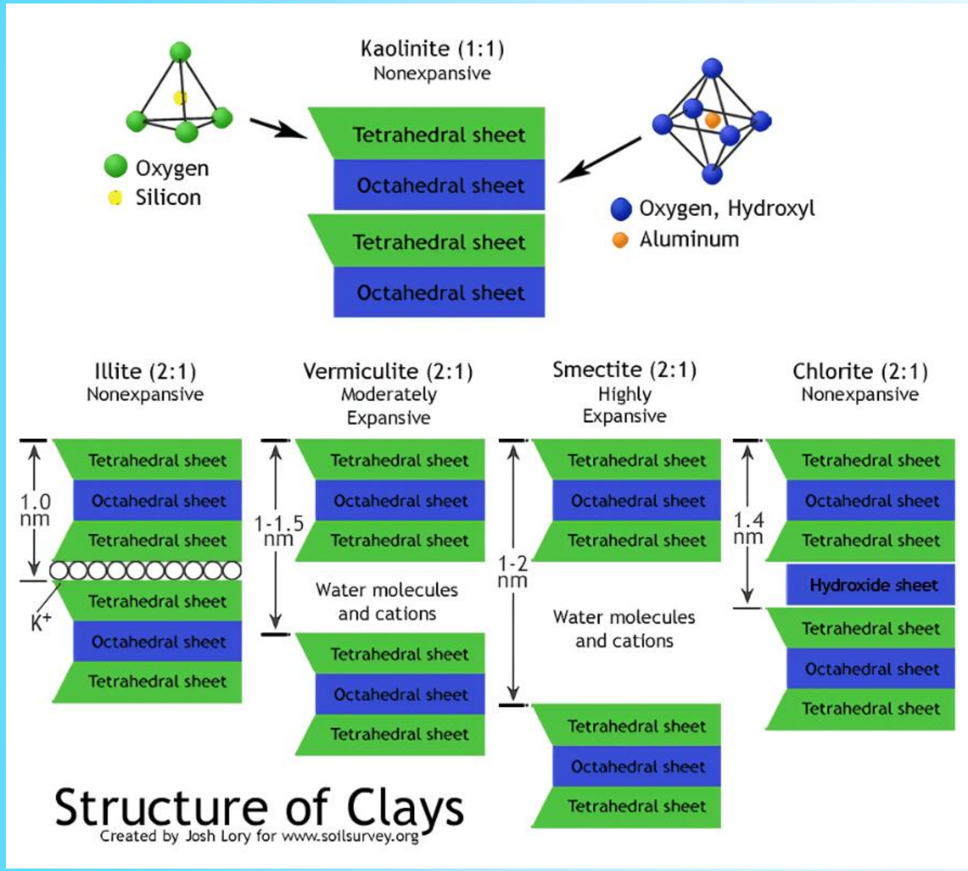
nano-sized Mgt (25-30 nm)

two-steps reduction starting at T>~450°C:

$Fe_3O_4 \rightarrow FeO \rightarrow Fe$

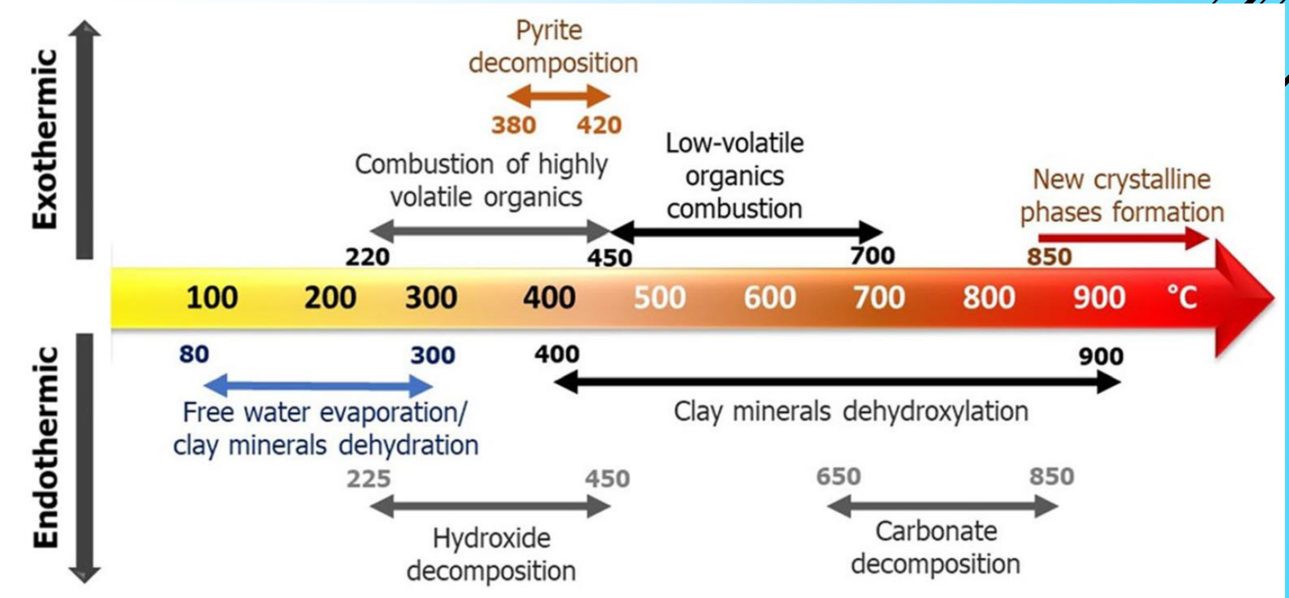
CLAY MINERALS AND FIRING

PHYLLOSILICATES



HEATING

- dehydration
- oxidation
- dehydroxylation
- decomposition and formation of new phases
- vitrification



✍ Clay particles: particles with a particle size of less than 20 μm

✍ Iron is present also as structural form on clay mineral and may occur in both the octahedral and tetrahedral sheets of 1:1 and 2:1 clay minerals

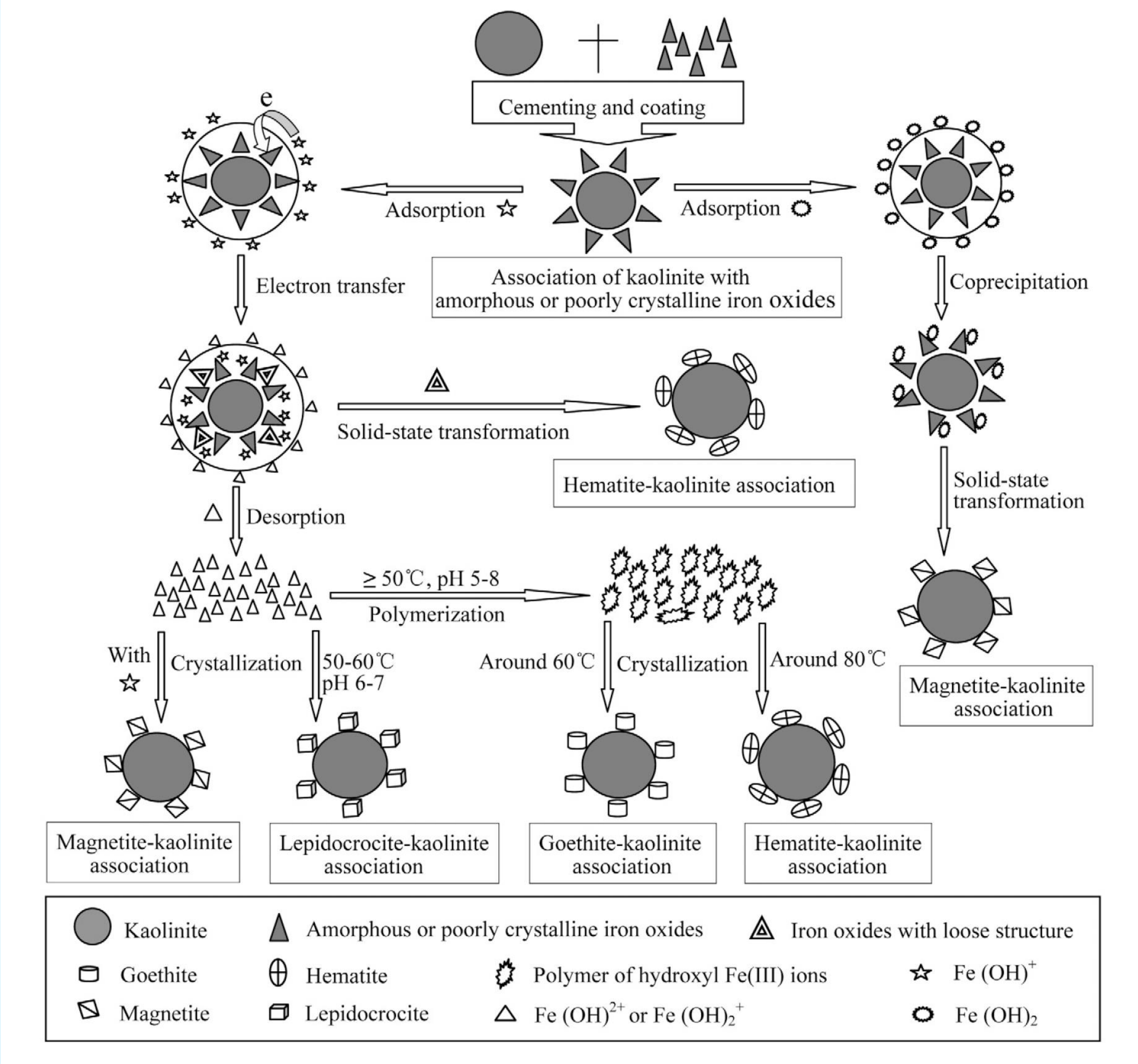
Source: Hanein et al, 2022. Materials and Structures (2022) 55:3

GOING COMPLICATED: CLAY + IRON (HYDR)OXIDE MIXTURE

- Clay materials can contain up to 15 wt. % of iron oxide phases
- Contents above 5% Fe_2O_3 promote a reddish or pinkish colour of clays
- Due to the high surface reactivity, clay minerals can affect the transformation process and product features (e.g., size and morphology) of ferrihydrite.

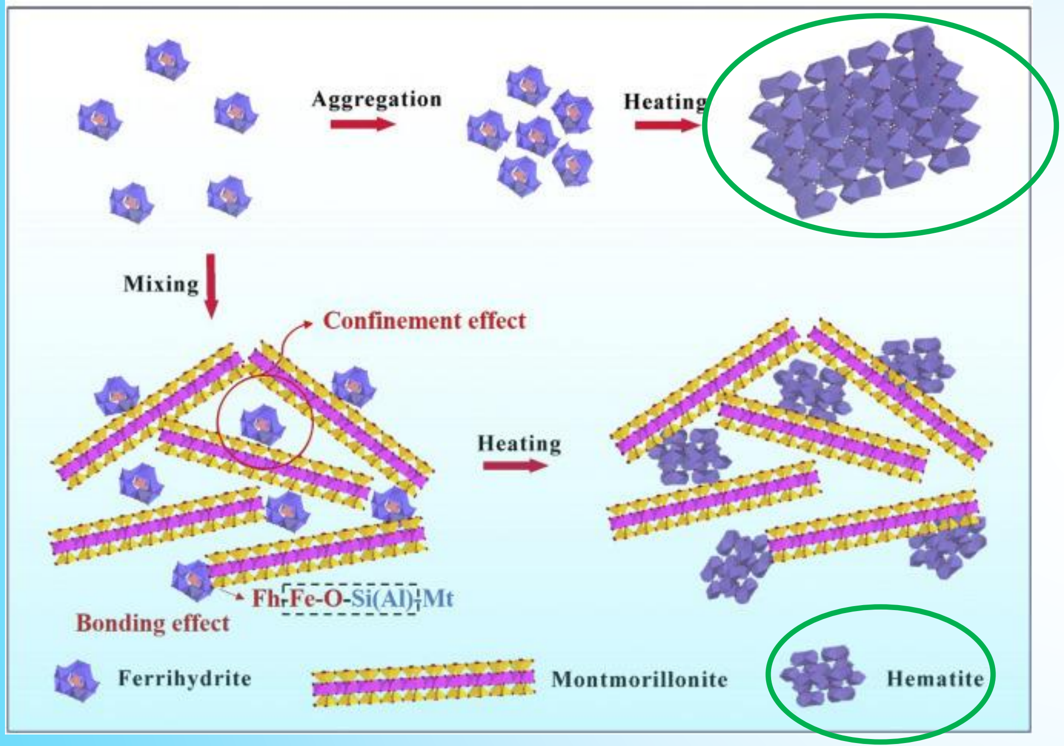
KAOLINITE + IRON OXIDE: possible transformations

Kaolinite
the most often used clay mineral in pottery production



Source: Wei et al., 2011. Soil Sci. Soc. Am. J. 75:45–55

MONTMORILLONITE + FERRIHYDRITE: heating in air



Source: Yan et al.,2021. Applied Clay Science 202, 105962

Montmorillonite disperses Fh and inhibit the formation of large aggregates in the mixing and heating process.

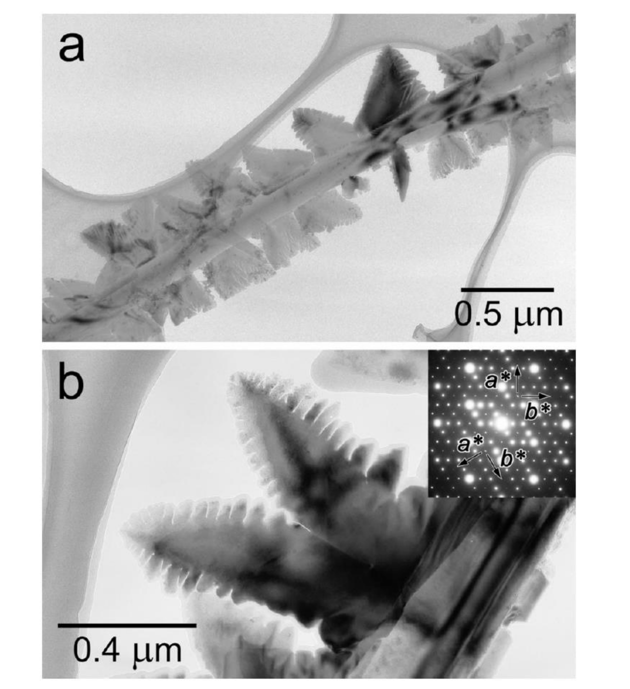
Montmorillonite could interact with Fh by the formation of Si−O−Fe and Al−O−Fe bonds.

The coexisting Montmorillonite significantly *decreased the size of Hem* particles under high-temperature conditions.

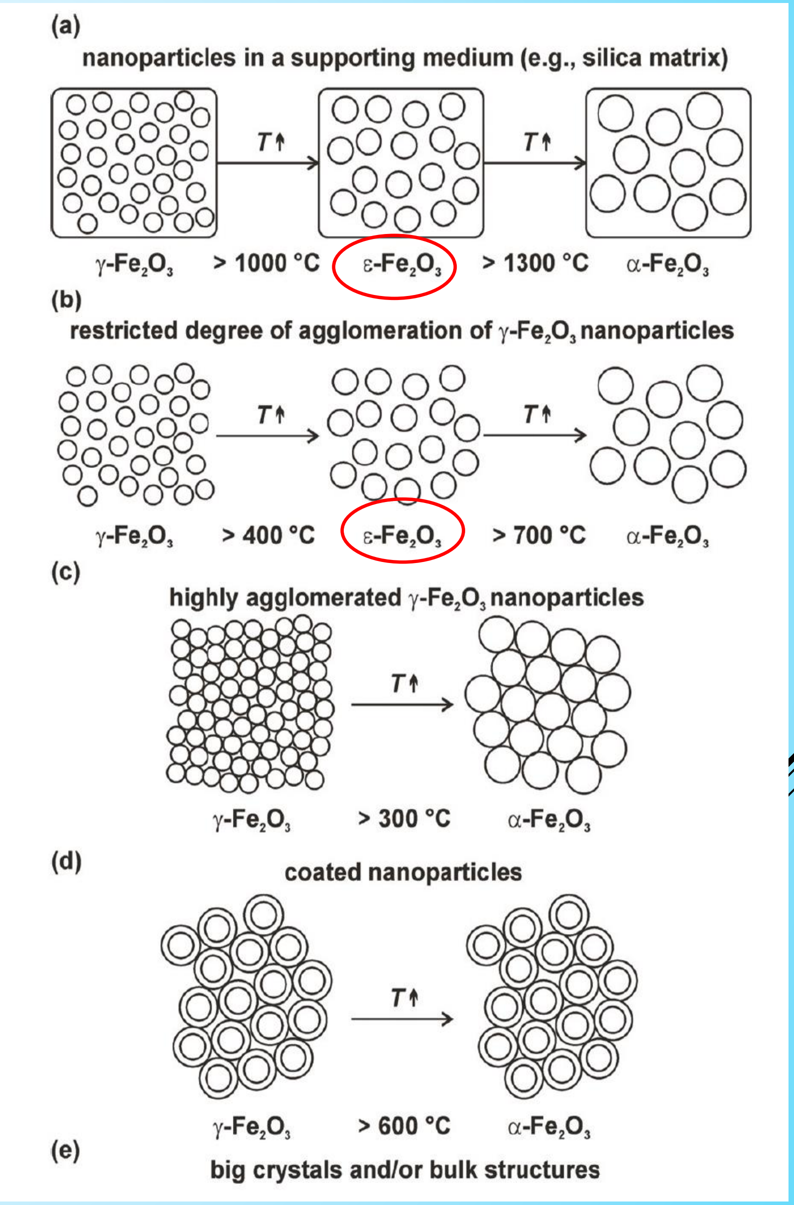
Maghemite nanoparticles in Silica matrix: heating products

ε-Fe_2O_3:
High temperature transformation product of maghemite nanoparticles, dispersed in Si-matrix

ε-Fe_2O_3 found in archaeological ceramics fired at very high temperatures



TEM images of ε-Fe_2O_3 crystals from ceramic sample from Japan (Kusano et al., Chem. Mater. 2008, 20, 151–156)



Source: Machala et al., 2011. Chem. Mater. 23, 3255–3272

THERMAL TRANSFORMATIONS IN ROCK-FORMING Fe-containing MINERALS

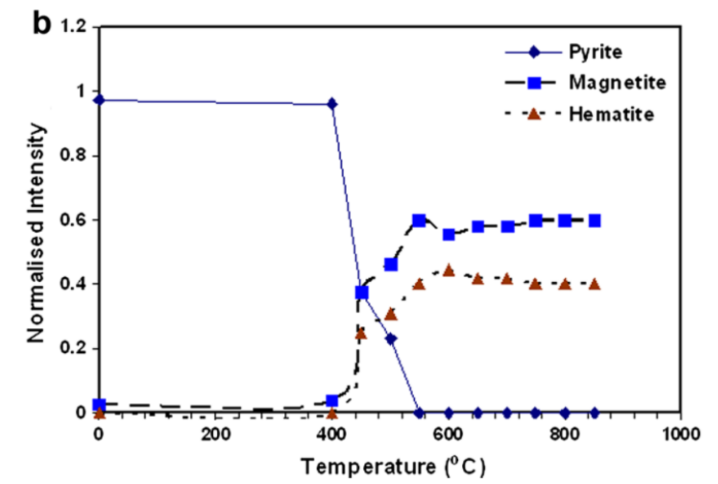
PYRITE (FeS_2) TRANSFORMATIONS

Heating in air:

$2FeS_2 + 51/2\ O_2 \rightarrow Fe_2O_3 + 4\ SO_2$

$3\ Fe_2O_3 + 8\ O_2 \rightarrow Fe_3O_4 + 6\ SO_2$

Reaction products: hematite, magnetite



Source: Bhargava et al., 2009, Fuel 88, 988–993

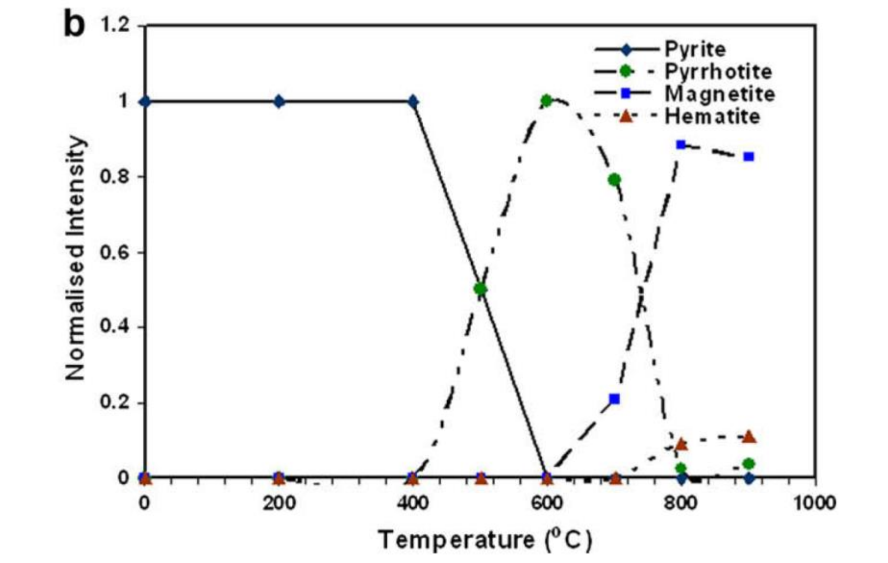
Heating in CO_2:

$$FeS_2 + 2CO_2(g) \leftrightarrow Fe_{1-x}S + 2CO(g) + SO_2(g)$$

$$7FeS_2 + 2SO_2(g) \rightarrow Fe_7S_8 + 2O2(g) + 8S$$

$$Fe_7S_8 + 2SO_2(g) + 4S \rightarrow 7FeS_2 + 2O_2(g)$$

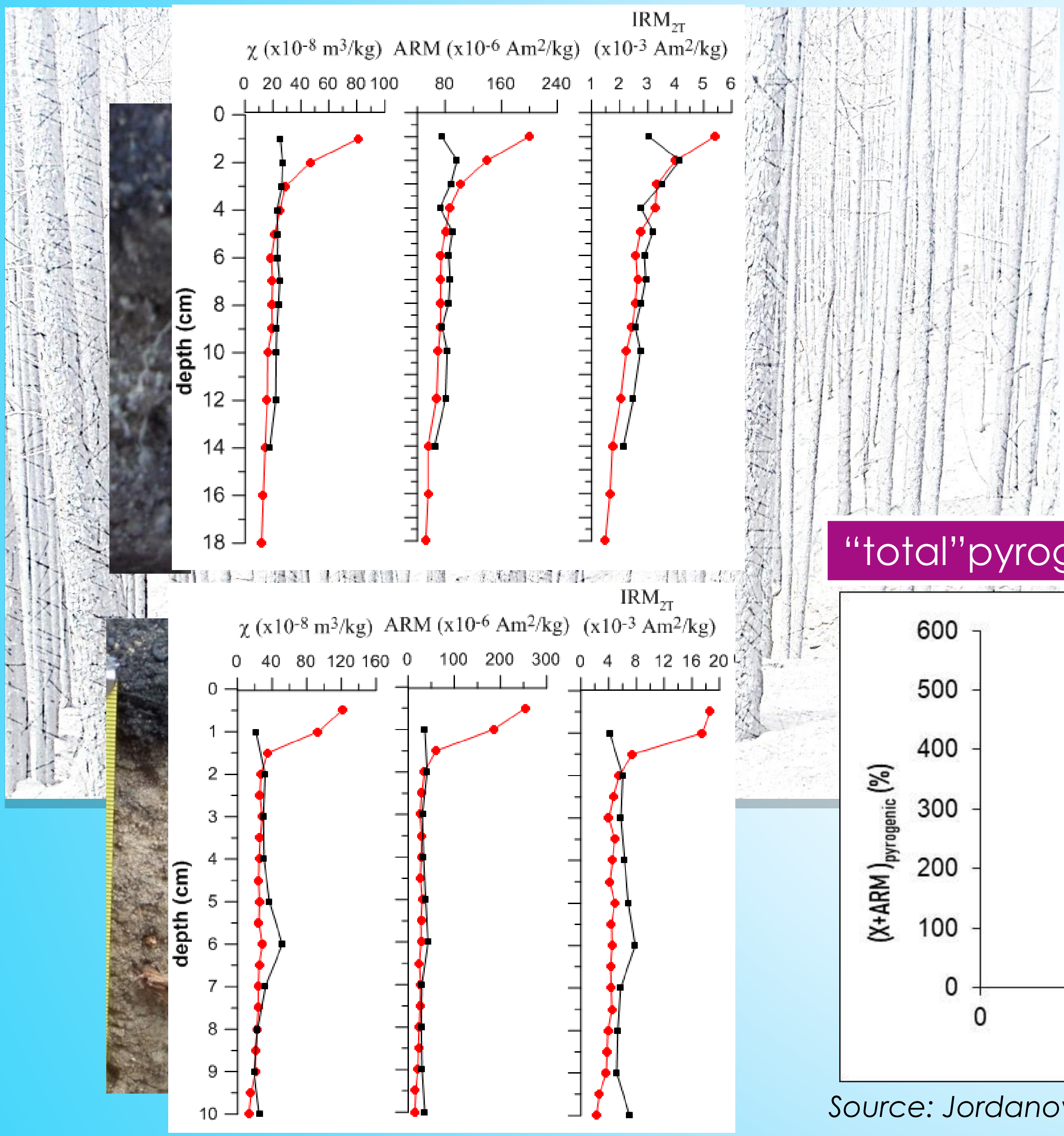
$$24FeS_2 + 7SO_2(g) \rightarrow 2Fe_7S_8 + 2Fe_3O_4 + 2Fe_2O_3 + 39S$$



PART 4

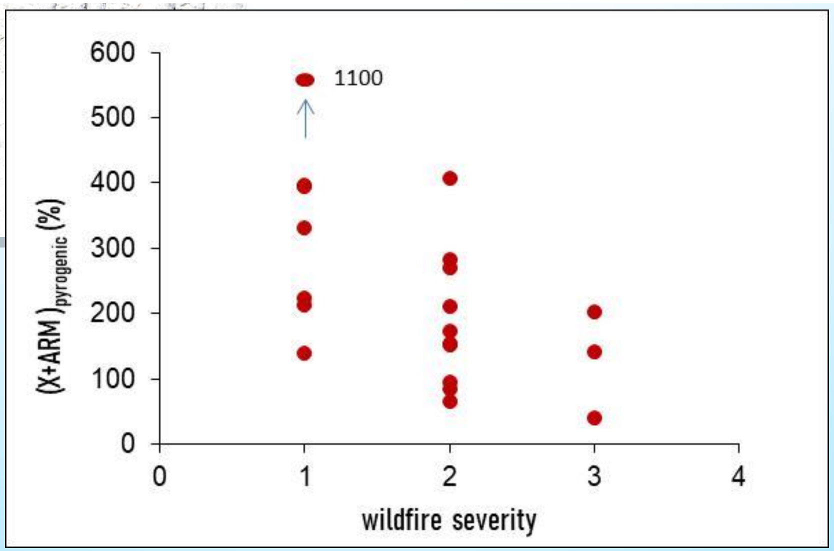
WILDFIRES and magnetic expression of FIRE SIGNATURE in natural soils

Wildfires and effects on magnetic properties of soil



- Strong magnetic enhancement of the uppermost 2-3cm in the burnt soil
- Both magnetic susceptibility and anhysteretic remanence increase significantly.
- Main pyrogenic magnetic mineral – magnetite

“total”pyrogenic magnetic enhancement



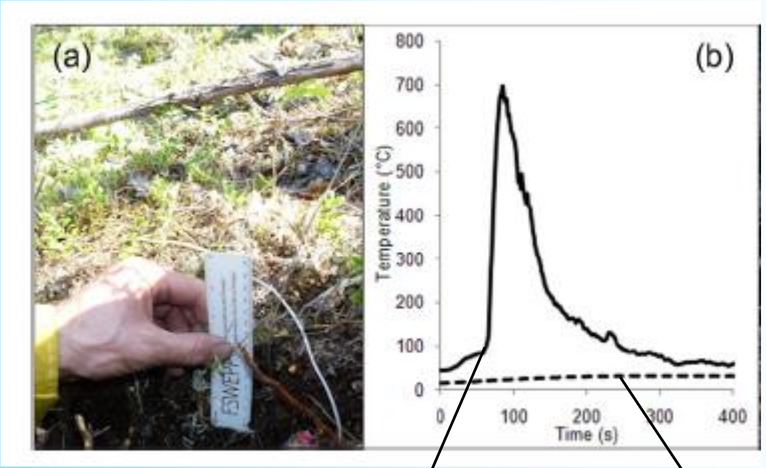
Source: *Jordanova et al, 2019. Land Degradation and Development, 30(18), 2226–2242*

Experimental forest firing – major findings

from Santín et al. (2016, Geoderma, 264, 71-80)

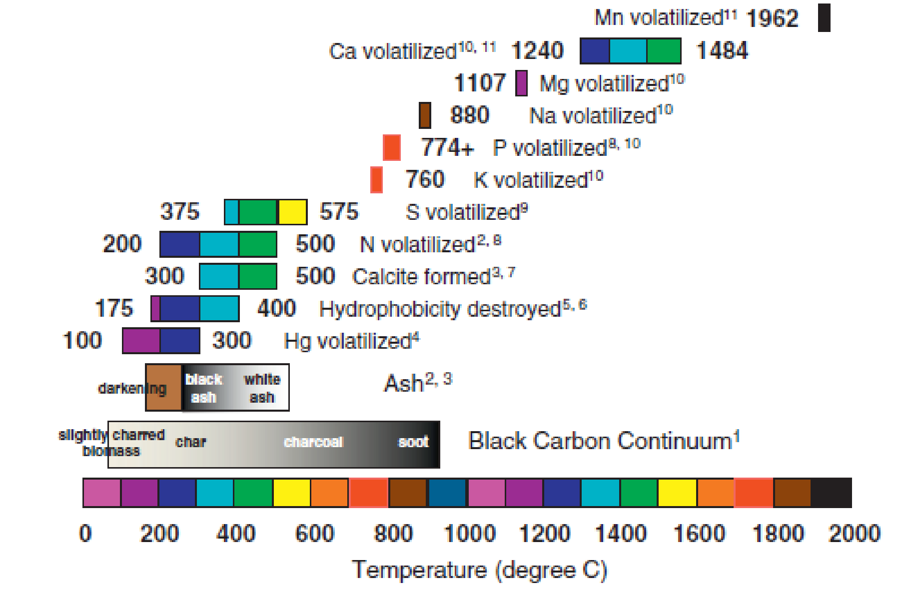
from Bodí et al. (2014, Earth Sci. Rev., 130, 103-127)

Boreal Forest fire

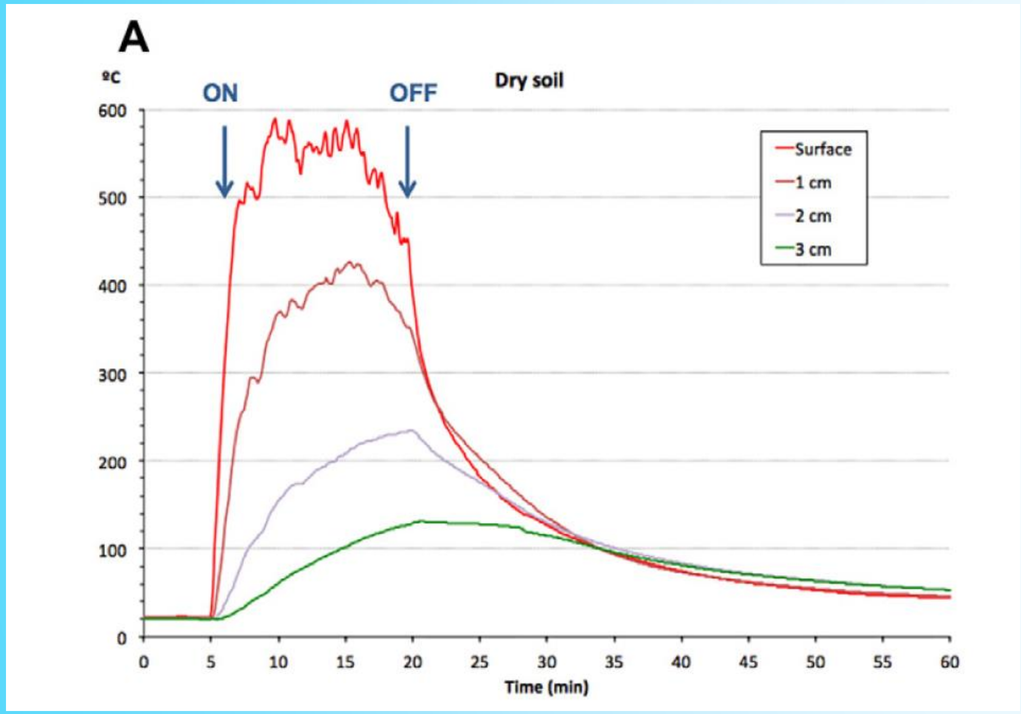


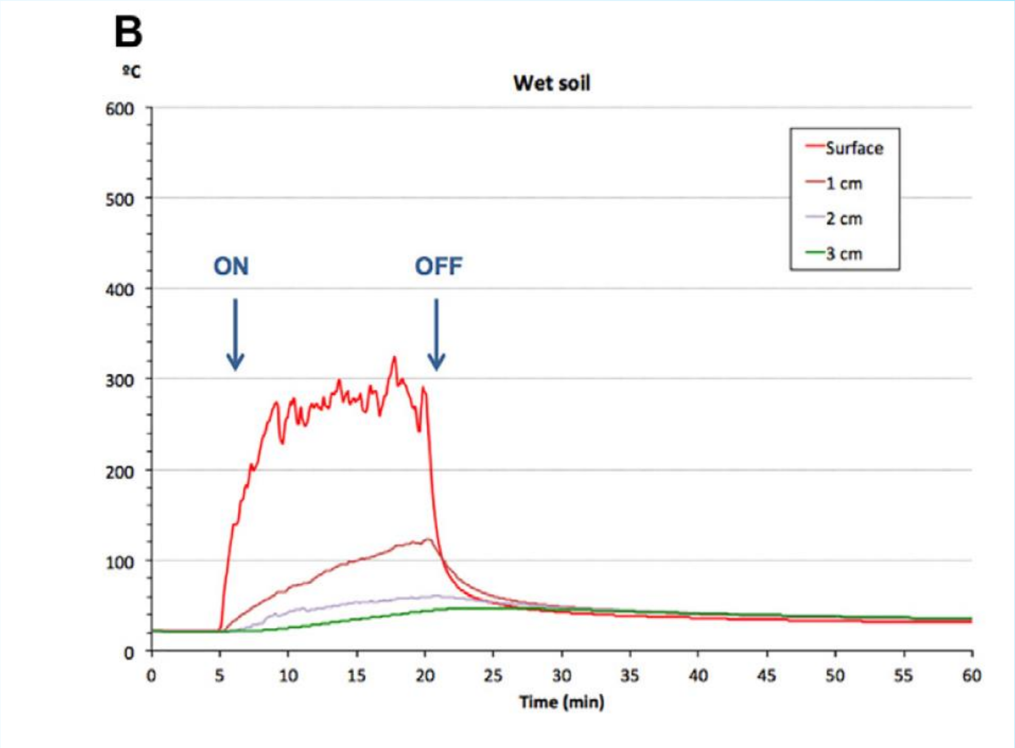
Forest floor surface

Forest floor/mineral soil interface



Temperature behavior on the surface and at the first centimeters of depth of a burned mollic topsoil under contrasted soil moisture content *(D. Badía et al. / Science of the Total Environment 601–602 (2017) 1119–1128)*





- Tmax and the heating duration are significantly lower in the wet soil than in air-dried soil in the first and second centimeters of depth
- soil heating is slower and cooling faster in wet soils as compared to dry soils

PART 5

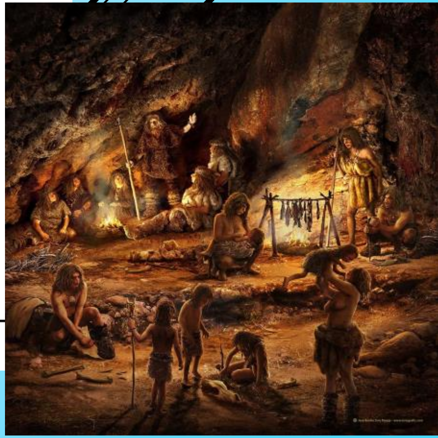
ARCHAEOLOGICAL BURNT CLAY: effects of heating on the magnetic signature

Evidence for first controlled use of fire by humans

From: Jha et al., 2021. Palaeo3, 562, 110151

Compilation of controlled use of fire by the prehistoric humans from major archaeological sites around the world.

Country	Archaeological site	Type of evidence	Age	Prehistoric phase boundary	References
India	Belan valley, Uttar Pradesh	Macroscopic charcoal	~55–50 ka	Middle Paleolithic	Present study
	Belan valley, Uttar Pradesh	Hearth ($n = 11$)	~18–10 ka	Epi-Paleolithic to Late Mesolithic	Misra (2002)
	Pratappur, Odisha	Charcoal	~17.9 ka	Late Upper Paleolithic	Patnaik et al. (2019)
	Karnool Cave, Andhra Pradesh	Hearths ($n = 1$)	~17.4 ka	Late Upper Paleolithic	Nambi and Murty (1983)
China	Zhoukoudian	Burnt stones, bones and charcoal fragments	~462 ± 45 ka	Late Lower Paleolithic	Weiner et al. (1998)
Israel	Gesher Benot Ya'aqov	Burnt seeds, wood, and flint	~790 ka	Lower Paleolithic	Goren-Inbar et al. (2004)
	Tabun/Hayonim Oumm Qatafa	Hearths, Charcoal	~200–100 ka	Early Middle Paleolithic	Mercier et al. (1995)
	Qesem Cave	Burnt bone, heated soil lumps, wood-ash	~400–200 ka	Late Lower Paleolithic	Karkanas et al. (2007)
South Africa	Pinnacle Point	Burnt tools	~164 ka	Early Middle Paleolithic,	Brown et al. (2009)
	Wonderwerk Cave	Burnt bone and ashed plant	~1.0 Ma	Lower Paleolithic	Berna et al. (2012)
	Swartkrans cave	Burnt bones	~1.0–1.5 Ma	Lower Paleolithic	Brain and Sillent (1988)
United Kingdom	Beeches Pit, West Stow	Burnt flint and bones	~414 ± 30 ka	Late Lower Paleolithic	Preece et al. (2006)
Germany	Schöningen	Burnt bone and sediment	~500 ka	Late Lower Paleolithic	Thieme (1997)
	Bilzingsleben	Burnt bone and sediment	~370 ka	Late Lower Paleolithic	Mania and Mania (2005)
France	Grotte XVI, Dordogne	Ash and burnt bones	~60 ka	Late Middle Paleolithic	Karkanas et al. (2002).
Spain	Bolomor Cave (Valencia)	Hearth	~228 ± 53 ka	Early Middle Paleolithic	Peris et al. (2012)
Australia	Lynch's Crater (North Queensland)	Charcoal	~45 ka	Late Middle Paleolithic	Turney et al. (2001)
Kenya	FxJj20, Koobi Fora	Burnt artefacts	~1.6 Ma	Lower Paleolithic	Gowlett et al. (1981)
Indonesia	Liang Bua, Flores	Ash and charcoal	~41 ka	Late Middle Paleolithic	Morley et al. (2017).
Malaysia	Great Cave of Niah, Sarawak	Charcoal	~43 ka	Late Middle Paleolithic	Stephens et al. (2005)
Philippines	Erne and Dalan Serkot Caves	Charcoal	~26 ka	Early Upper Paleolithic	Mijares and Lewis (2009)



Detecting controlled use of fire by humans

- most ancient use of fire → in nomadic societies: occasional use of open air fireplace may destroy the charcoals, thus problematic to find definite evidence
- progressively less nomadic life-style (e.g. larger population) → more intensive site use → better opportunity for charcoal preservation
- Major criteria for reliable detection of fire use by ancient humans: ❶ fireplaces/hearths in association with burnt bones, sediments, etc; ❷ *in situ* presence of wood ash in a cave where trees are not normally found; ❸ burnt bones and macroscopic charcoal associated with lithics in a stratigraphic unit/layer; ❹ presence of burnt materials (e.g., charcoal, bones, stones) dispersed in a depositional context

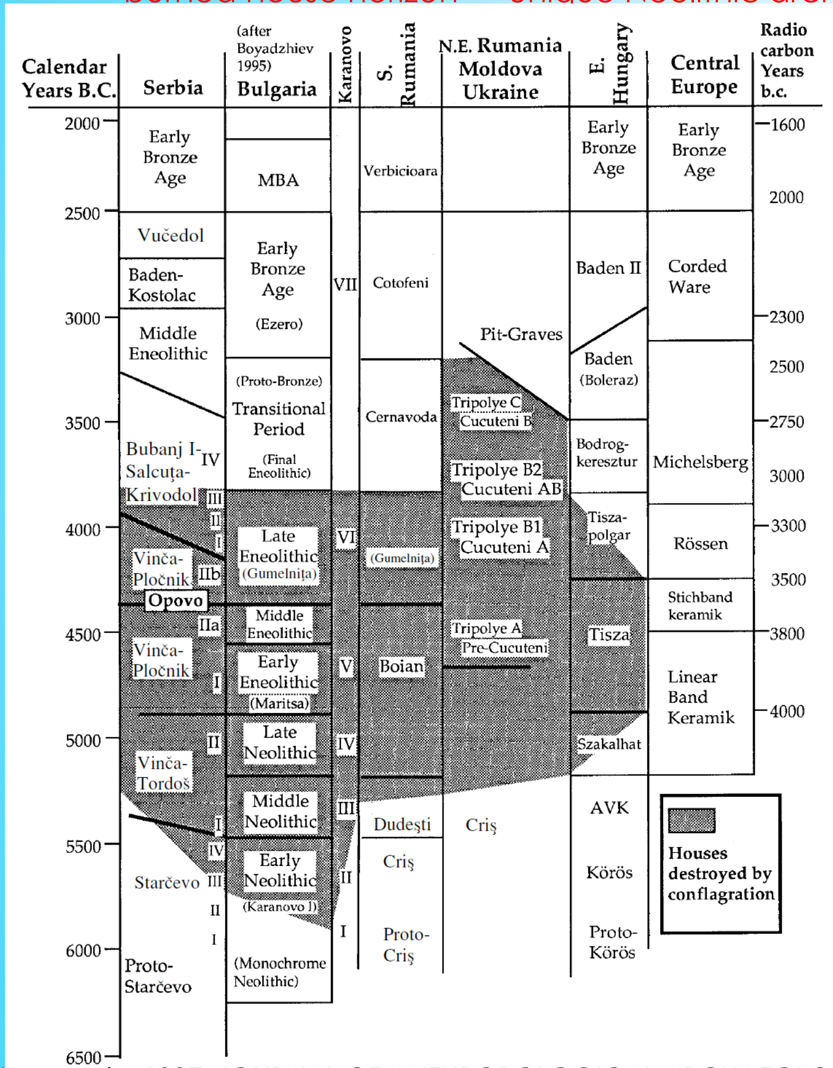
Fire - accepted as an essential component of human life for:

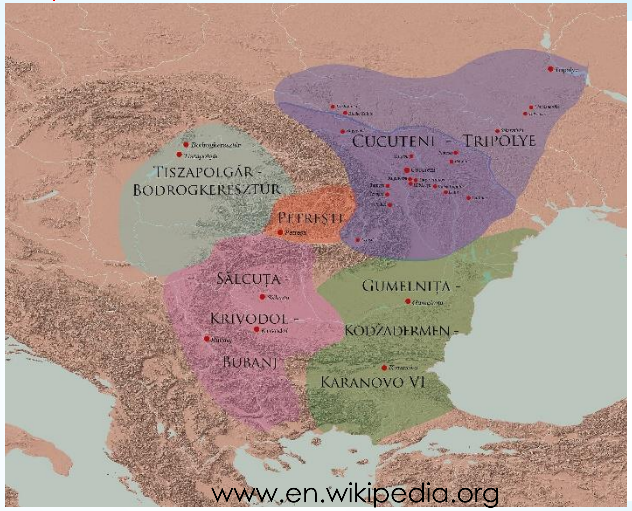
- development of resources
- protection from animals and cooking food
- advancement of tools preparation technology

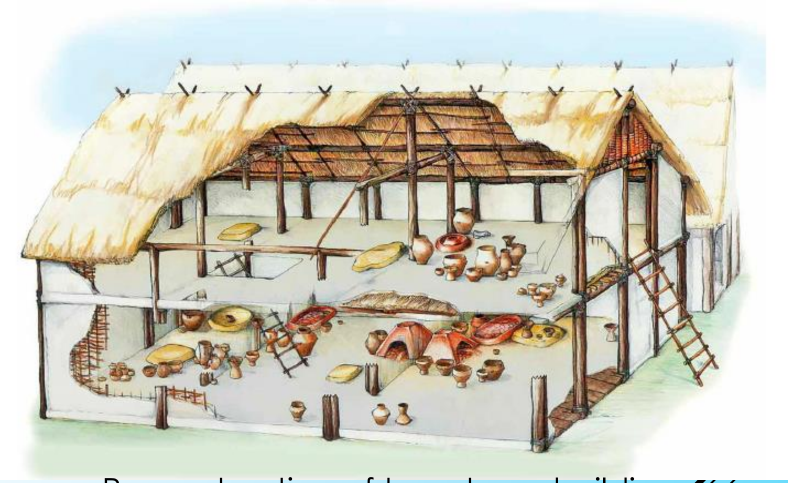
ARCHAEOLOGICAL BURNT CLAY

1. Remains from settlement's destruction by fire (conflagration event)

"burned house horizon" – unique Neolithic archaeological phenomenon in







Reconstruction of two-storey building (*source: Pál Raczky, 2014, The Oxford Handbook of Neolithic Europe*)

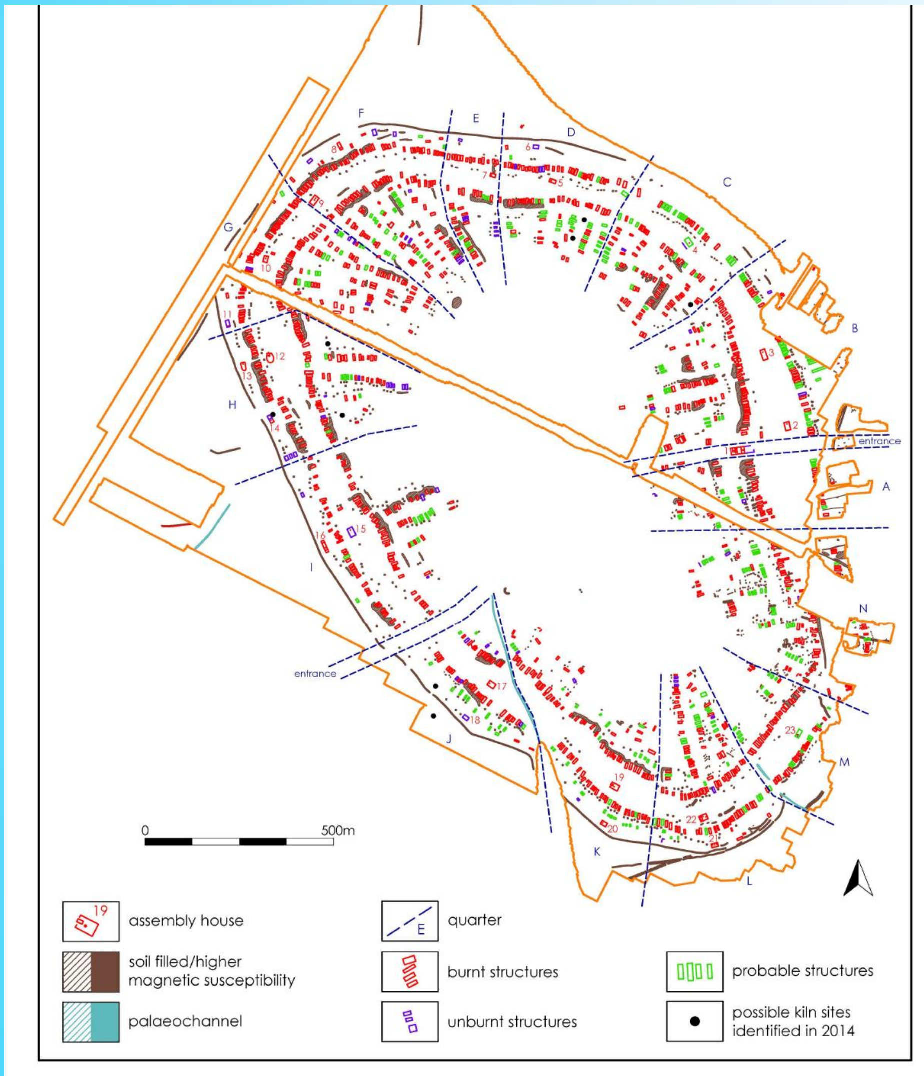
Experimental archaeology: combustion of a wattle and daub house, Vadastra 2006
Source: Gheorghiu, 2008; Documenta Praehistorica XXXV, 167-178

Stevanovic, 1997, JOURNAL OF ANTHROPOLOGICAL ARCHAEOLOGY 16, 334 – 395

The Trypillia megasites of Ukraine are the largest known settlements in 4th millennium BC in Europe

The largest reaches 320 ha in size – Nebelivka megasite

Source: Chapman et al., 2019, Front. Digit. Humanit. 6:10.



Major archaeological finds - burnt daub with imprints of wood

- Numerous burnt houses, including two-storey
- large public buildings ('mega-structure', "temple")
- fortifications

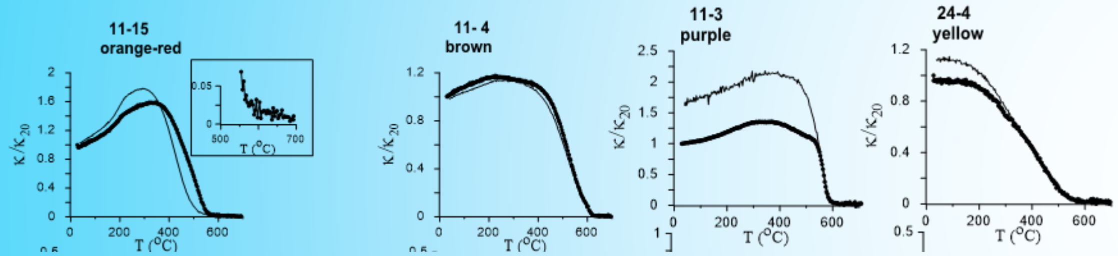
Source: Trypillia Mega-Sites and European Prehistory 4100-3400 BCE Eds. J. Müller, K. Rassmann and M. Videiko 2016. Routledge (Taylor & Francis Group), Themes in Contemporary Archaeology, volume 2, European Association of Archaeologists, pp.309; ISBN: 978-1-910-52602-6.

Neolithic site Mursalevo-Deveboaz from Bulgaria 5700 – 5000 BC)

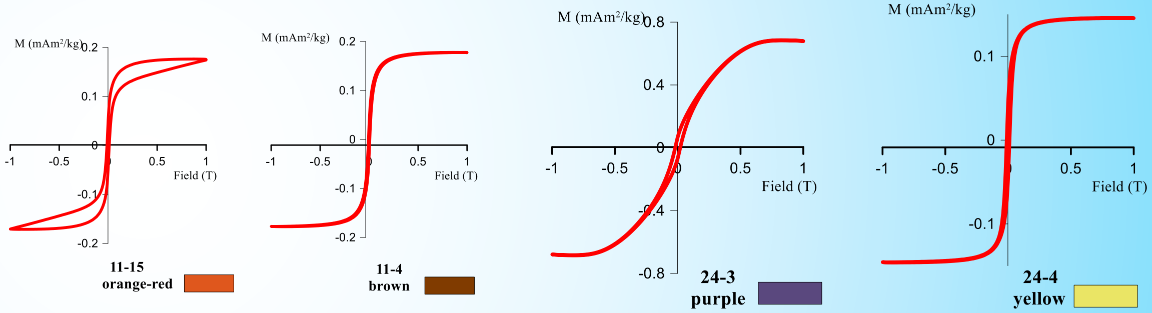
Area **20 000 m²** , **~ 60 houses**

Rock-magnetic study on a collection of 445 samples from 25 houses

Jordanova et al., 2018, Journal of Geophysical Research: Solid Earth, 123. Art. No 2017JB015190



Hysteresis loops



Magnetic minerals identified:
Magnetite / maghemite , Hematite

color dependent magnetic properties of daub

Sample No	color	Bc (mT)	Bcr (mT)	Ms (mAm²/kg)	Mrs (mAm²/kg)	Hysteresis loop shape	χ_{fd}%
11-3	purple	19.1	68.2	940.80	281.40	wwl	4
11-10	purple	7.8	16.6	819.48	185.52		3
11-11	purple	17.1	33.9	893.26	258.99		1
24-3	purple	19.8	55.9	679.57	68.02	pot-belly	2
24-4	yellow	10.9	20.6	145.67	45.27		3
24-12	yellow/light brown	6.8	43.4	226.8	29.2	wwl	10
11-15	orange-red	11.5	39.3	173.45	49.27	wwl	12
24-5	orange-red	10.5	32.8	241.63	67.22	wwl	12
17-12	orange-red	10.9	34.8	433.10	93.14	wwl	11
11-4	brown	6.7	18.9	177.48	32.71		6

Magnetite SD/PSD

Magnetite SP/SD

Magnetite/maghemite
SP+SD
Hematite

Magnetite SD

2. BRICKS

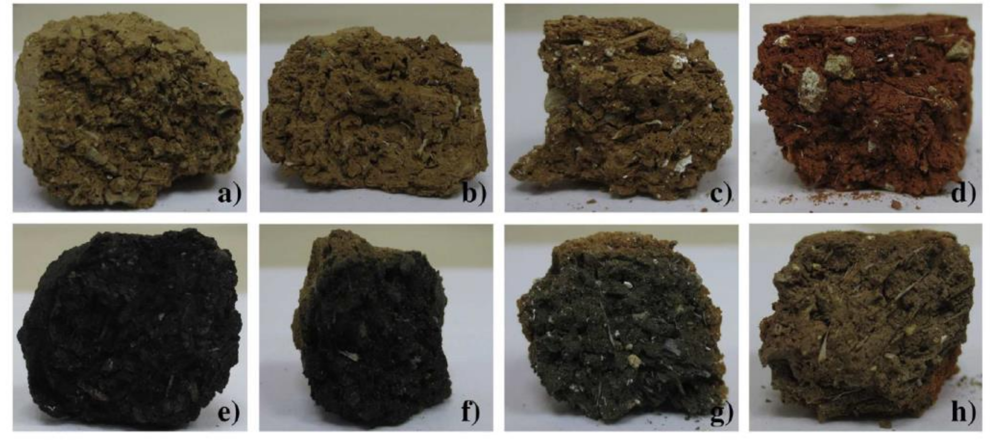
Mud-bricks for construction of houses in the Near East and Eurasia from the Neolithic to modern times
Mud brick - chaff-tempered, sun-dried mechanically formed sediment

Burned mud-brick walls of an Bronze Age site from Crete
Source: Maud Devolder et Marta Lorenzon, « Minoan Master Builders? », Bulletin de correspondance hellénique [En ligne], 143.1 | 2019, mis en ligne le 01 août 2020, consulté le 16 mars 2022. URL : http://journals.openedition.org/bch/718 ; DOI : https://doi.org/10.4000/bch.718

RECONSTRUCTION OF ENVIRONMENTAL FACTORS INFLUENCING THE APPEARANCE OF MUD BRICKS IN ARCHAEOLOGICAL CONFLAGRATION EVENTS

Forget et al., 2015; Journal of Archaeological Science: Reports 2, 80–93

Experimental mud-bricks heated at: 500, 600, 700 and 800°C



In oxidising conditions

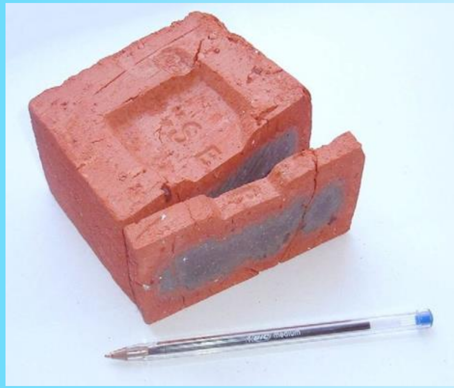
In reducing conditions

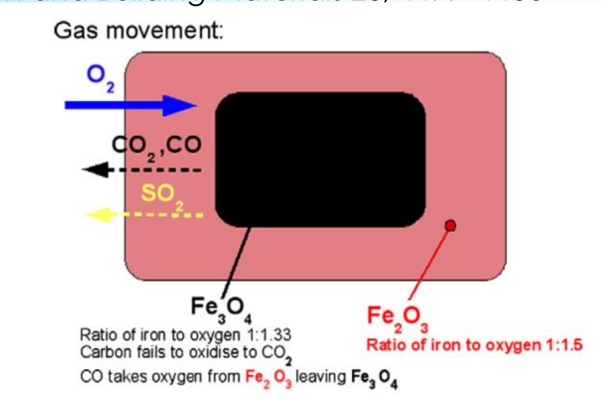
Clay bricks

For the production of heavy clay bricks the raw clay is mined, shaped into a brick in an extruder, dried to evaporate the water, and then fired in a kiln at a temperature typically between 900 and 1050 °C.

The black reduction core in heavy clay ceramics is a typical feature of clay bricks.

Source: Gredmaier et al., 2011, Construction and Building Materials 25, 4477–4486



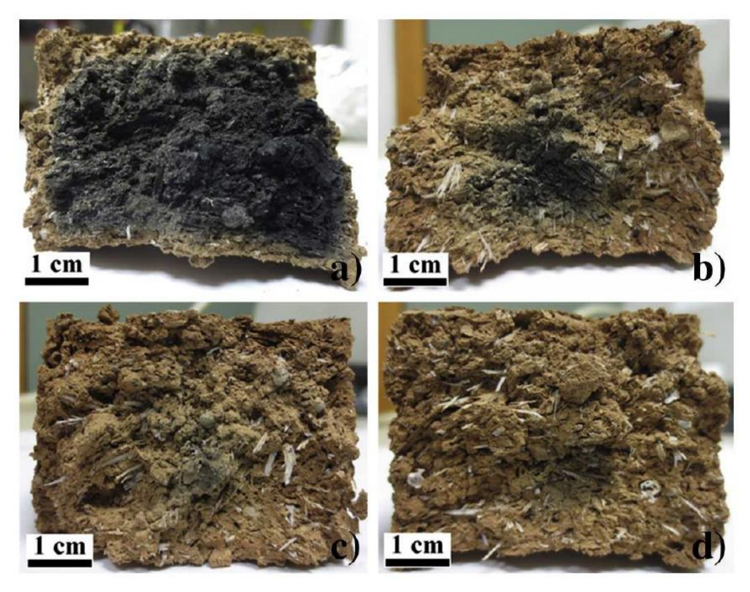


CO2, CO, SO2 and water vapour are gases that develop during firing of clay

The following factors determine the extent of black reduction coring in fired clay ware:

❶Firing time – a longer firing time can eliminate the black reduction core.
❷ The oxygen atmosphere during firing. Lack of oxygen promotes the formation of black reduction cores.
❸ Iron oxide content in the raw clay.
❹ Carbon content and burnout or oxidation of carbon during firing of the raw clay.
❺Fineness of clay and degree of compaction. Gas exchange and gas development are different between clay powder and an extruded brick

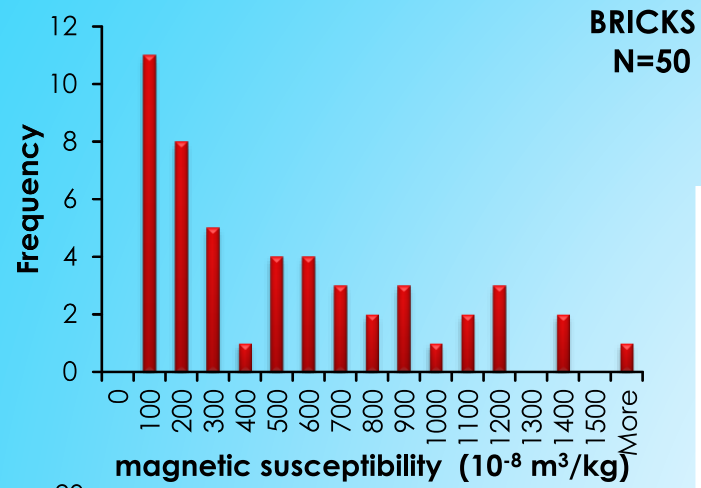
Archaeological bricks are normally fired in a continuous oven-type chamber. The maximum temperature practically attainable is 1100 °C after one week of burning *(Scalenghe et al., (2015) Quaternary International 357 189-206)*.

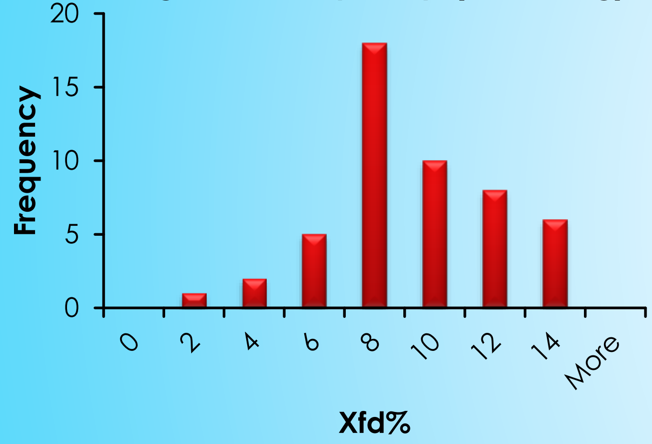


Experimental mud bricks fired at 600°C for time durations:
a)0 min, b) 15 min, c) 30 min, d)1 h

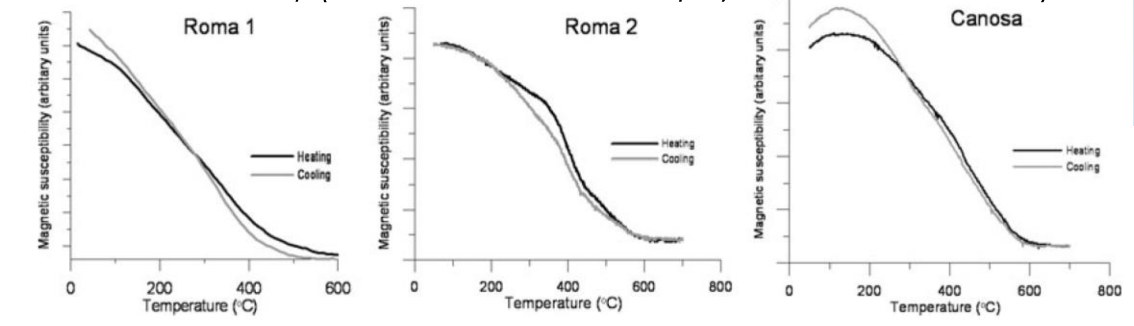
Source: Forget et al. 2015. Journal of Archaeological Science: Reports, 2, 80–93

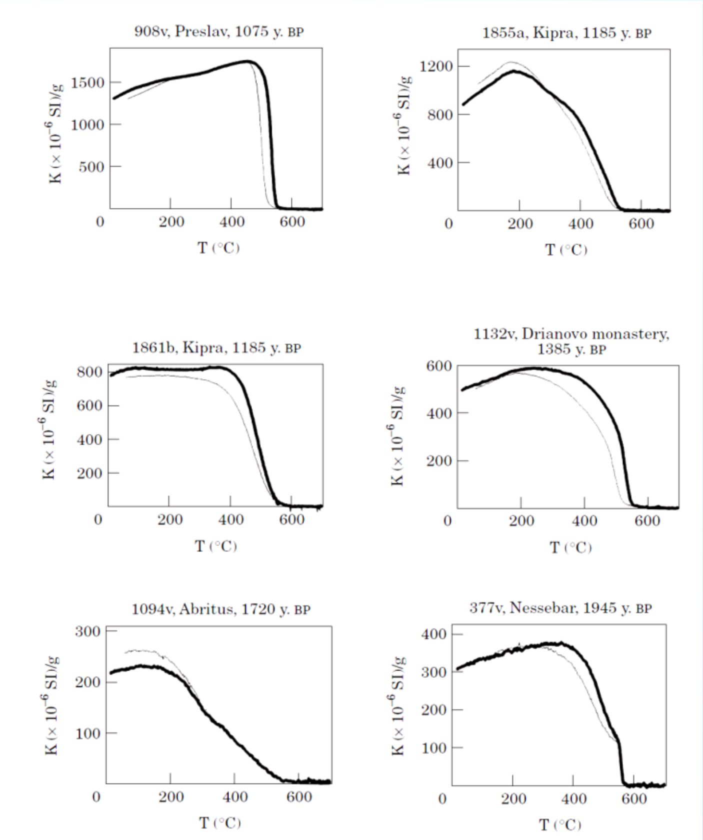
Rock magnetic properties of bricks



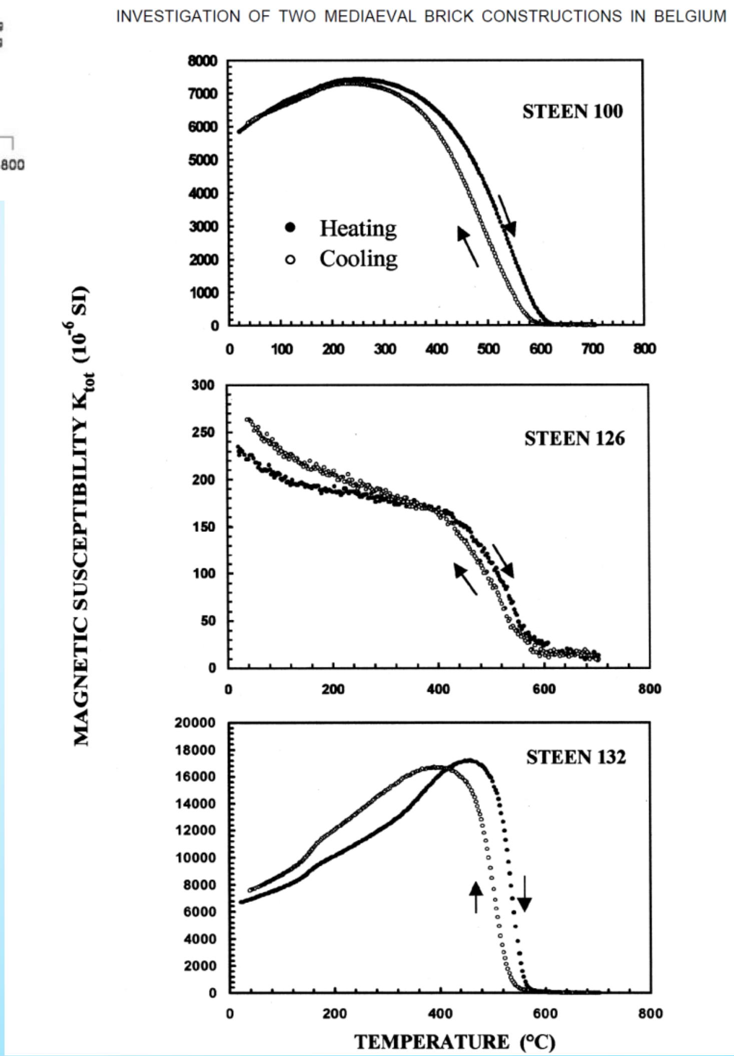


Bricks from Italy (*Tema et al., 2010, Geophys. J. Int.180, 596–608)*





Source: Hus et al., 2003. Geoarchaeology: An International Journal, 18 (2), 225–253

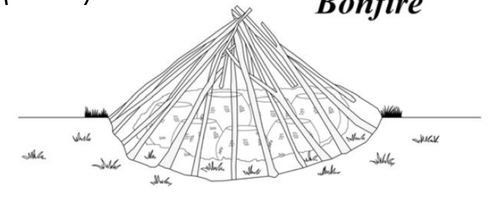


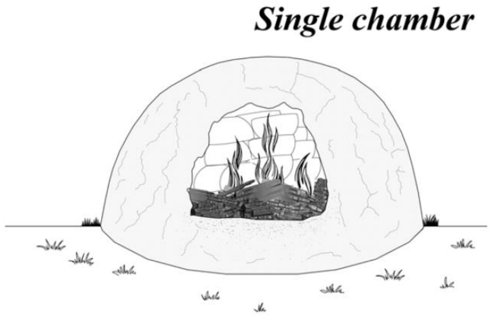
- ➢ firing produces significant portion of fine superparamagnetic grains during brick's production
- ➢ brick samples show stable susceptibility behaviour, suggesting sufficiently high temperatures achieved during their preparation.
- ➢ magnetite/titanomagnetite is the dominant ferrimagnetic phase
- ➢ minor changes on cooling suggest that the magnetic mineralogy is practically stabilized and no phase changes occur during heating to 700°C in air.

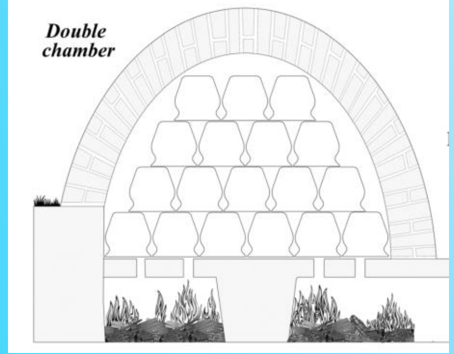
3. POTTERY

CERAMIC FIRING

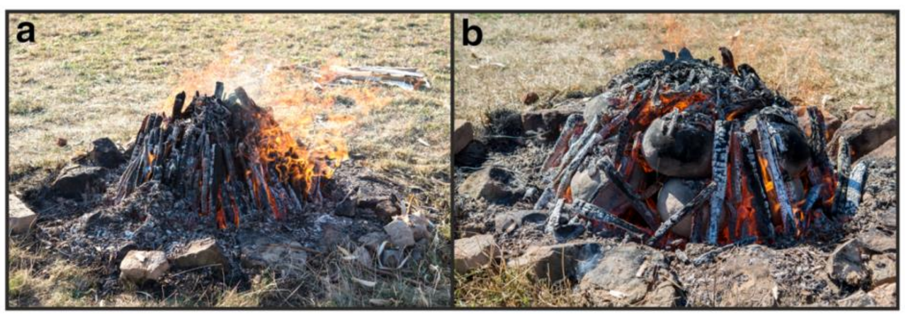
Source: Gliozzo, 2020. Archaeological and Anthropological Sciences (2020) 12:260

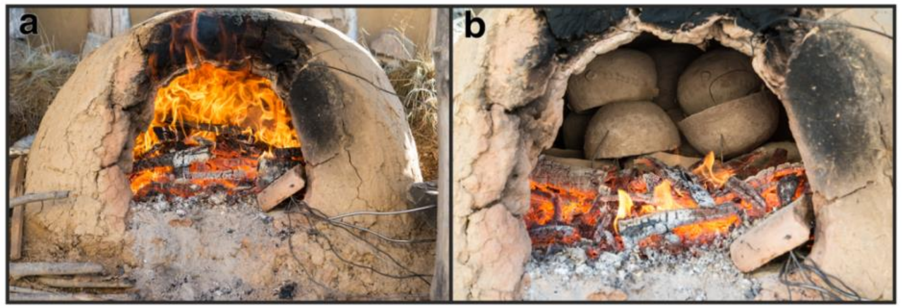






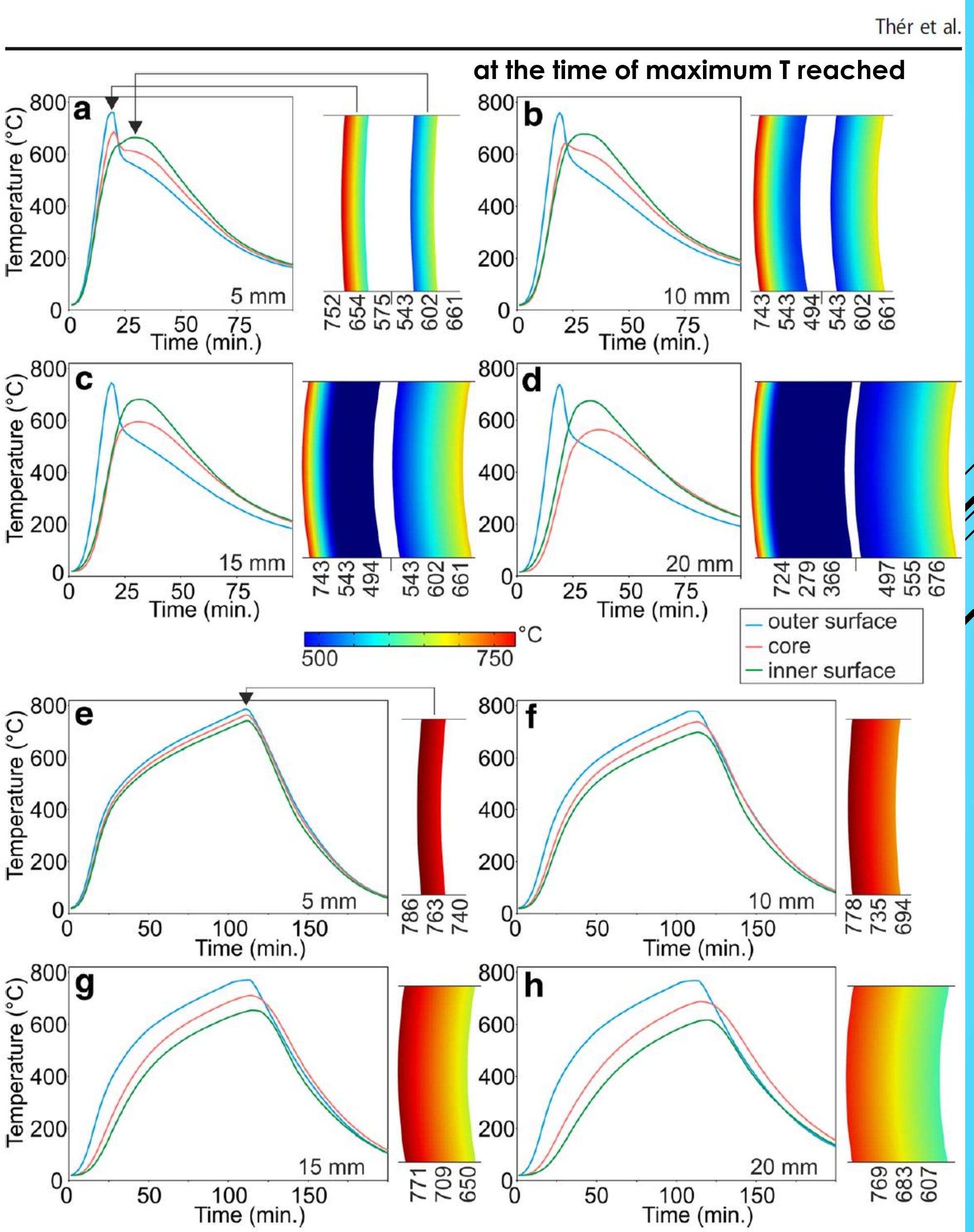
Source: Ther et al., Journal of Archaeological Method and Theory https://doi.org/10.1007/s10816-018-9407-x





kiln firing: firing using pyrotechnological installations characterized by a combustion chamber (firebox), where the fuel burns, and a firing chamber

open firing (non-kiln firing, bonfire): firing done in a small area, sometimes in a pit or depression partially excavated in the ground, without any permanent kiln structure; characterized by a short firing cycle, rapid heating rate and irregular temperature, non-uniform firing (i.e. local changes in redox conditions and temperature, which can vary by 100°C from place to place)
Source: Daszkiewicz and Maritan, 2016, The Oxford Handbook of Archaeological Ceramic Analysis



at the time of maximum T on the inner surface of the vessel

POTTERY FIRING TECHNIQUES

Source: Guo, (2017): Chinese Archaeology, 17, 179-186

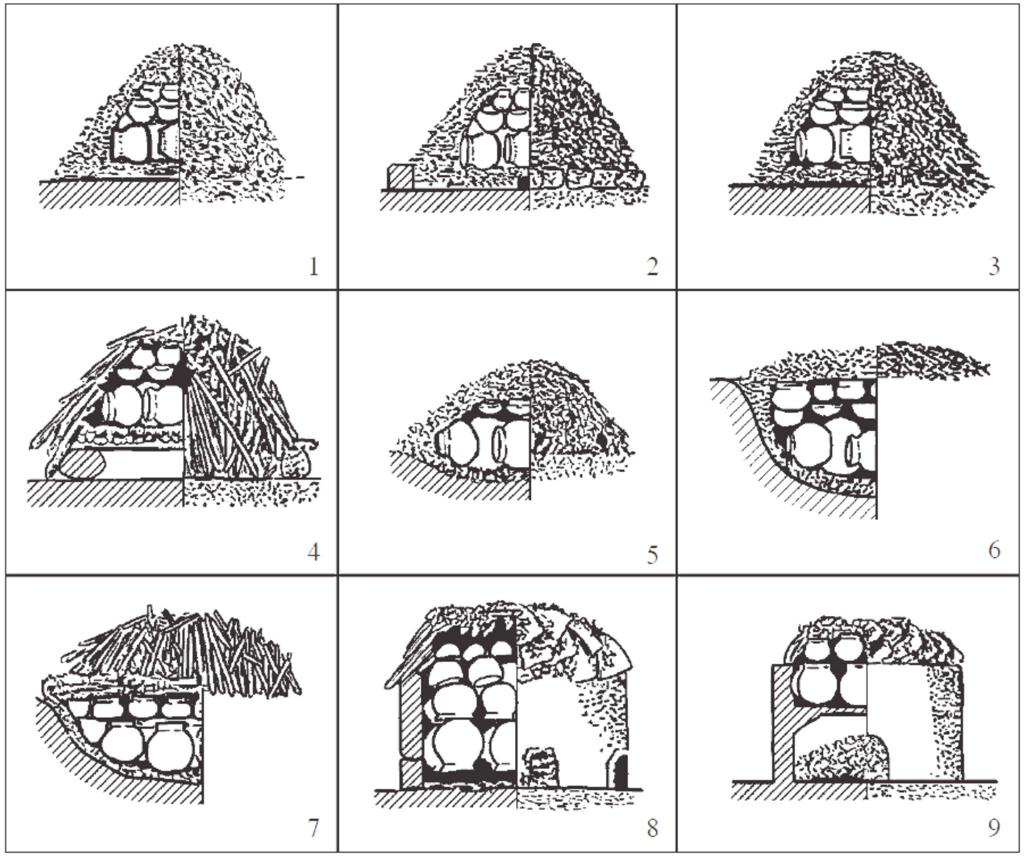


Figure 2 Pottery firing techniques in Africa.
1. Bonfire; 2. Surrounded bonfire; 3. Bonfire with fireproof materials separating the pots from the fuel; 4. Elevated bonfire; 5. Depression; 6. Pit; 7. Pit with fireproof materials separating the pots from the fuel; 8. Oven; 9. Updraft kiln (Quoted from Gosselain 1995:153, Figure 4).

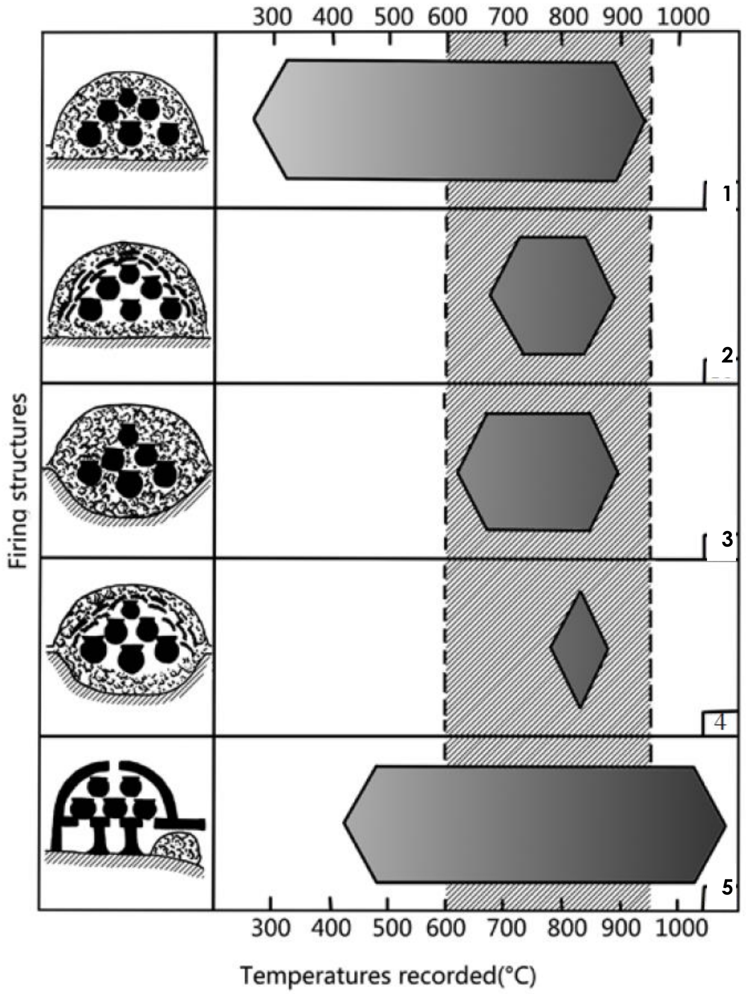
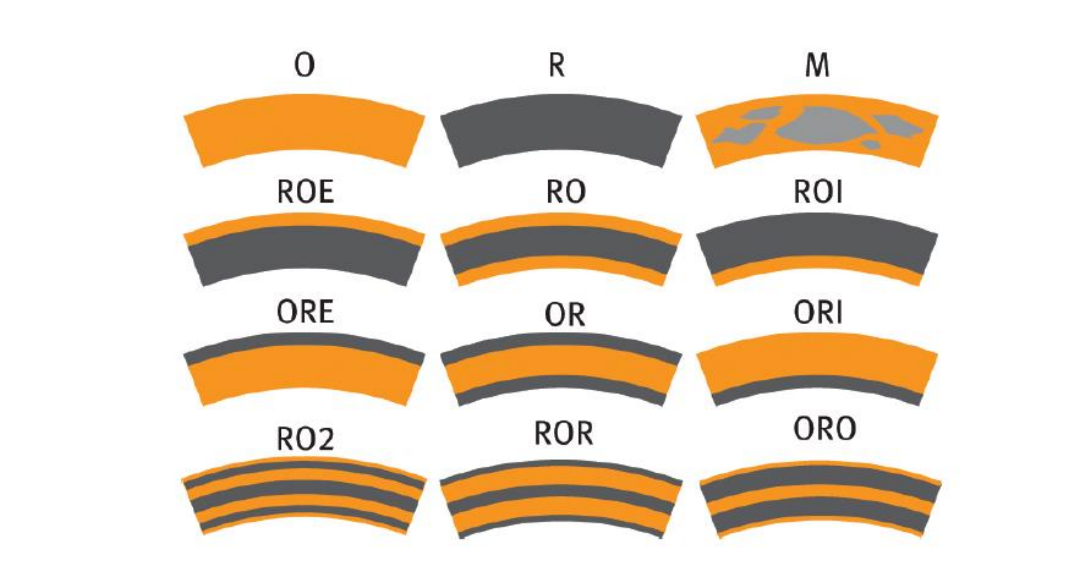


Figure 3 Temperature ranges for the five kinds of firing.
1. Open firing; 2. Open firing with potsherds covering the pots; 3. Pit firing; 4. Pit firing with potsherds covering the pots; 5. Updraft kiln firing (Quoted from Gosselain 1992:246).

- Fundamental difference between open-air firing structures and kilns
- bonfires lack insulation layer
- the clay layer of clay-shell ovens is very limited in its heat-preserving effects too
- The structure of pottery kilns provides temperature insulation and traps the heat inside.
- the main particularity of pottery kilns is the spatial separation of firing chamber and stacking chamber.
- Both characteristics have a positive effect on the performance of the kiln in firing pottery.
- Ceramic kilns can meet three major requirements of potters: controlling the firing atmosphere and temperature better, attaining higher temperatures, and improving fuel efficiency

Possible oxidation structures of pottery fabric, according to Eramo and Mangone *(2019, Physical Sciences Reviews, 20180014)*



O – oxidized domains
R – reduced domains
M – marbled structure
E – external
I – internal
Abbreviations from left to right denote sequence from the core to the pottery surface

Table 27.1 Basic atmospheric conditions during firing in antiquity (after Maggetti, 1991). Numerous variants are also possible

Type of firing		Heating-maintenance	Cooling
more ancient	A	reducing	oxidizing
↓	B	reducing	reducing
more recent	C	oxidizing	oxidizing

Source: Daszkiewicz and Maritan, 2016, The Oxford Handbook of Archaeological Ceramic Analysis

The presence of calcite in archeological ceramics

main types of ceramics

calcareous (calcite-rich) ceramics

siliceous (non-calcareous) ceramics

carbonate-rich clayey materials have a lower sintering temperature (~ 800 °C) than carbonate poor clayey materials, because Ca and Mg act as fluxes

calcite $CaCO_3 \xrightarrow{\sim 675–800°C} CaO + CO_2$

dolomite $CaMg(CO_3)_2 \xrightarrow{\sim 800°C} CaCO_3 + MgO + CO_2$

Maniatis et al., 1981, Journal of the American Ceramic Society 64 (5), 263-269

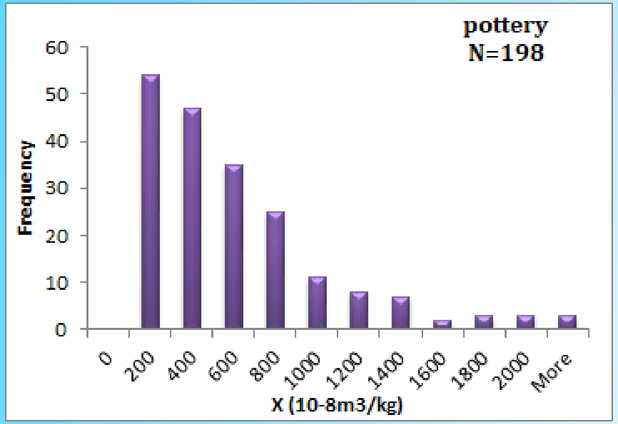
the role of Ca content of clays on the transformations of iron-containing phases on firing at 700°C to 1080°C.

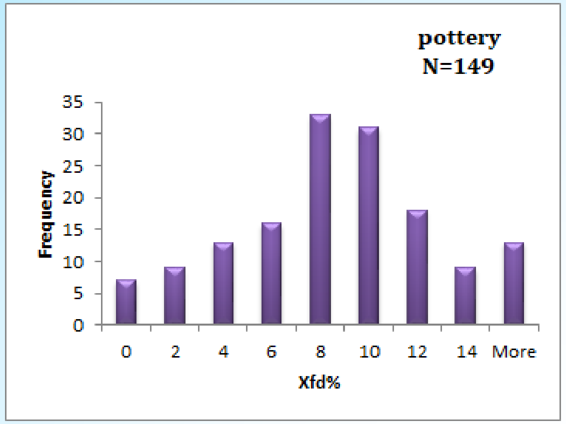
The main conclusions are:

(1) The particle size of magnetic iron oxides (mainly hematite) increases on firing at 700°C. At higher firing temperatures, the particle size increases continuously in noncalcareous clays, whereas it decreases appreciably at 1080°C in calcareous clays.

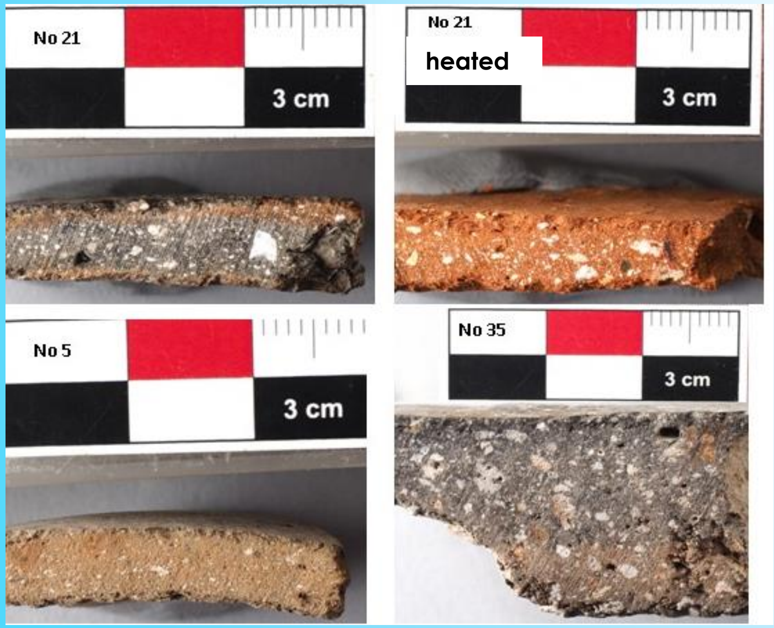
(2) The total amount of iron in magnetic phases is higher in noncalcareous than in calcareous clays fired at >700"C. This amount is determined from the iron oxides in the unfired clays and/or the contribution of the lattice iron on firing

Rock magnetic properties of pottery fragments

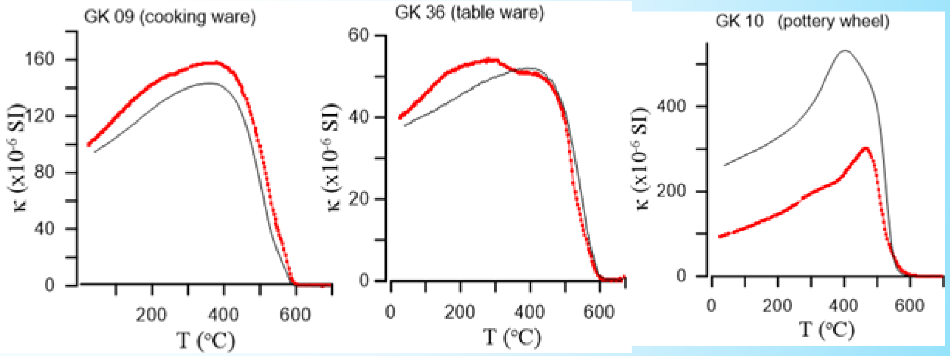




High content of strongly magnetic iron oxides
High relative share of ultra-fine SP particles



Pottery fragments from Iron Age site Gluhite kamani (Bulgaria)



Tc ~525°C

Tc ~580°C

Tc~514°C

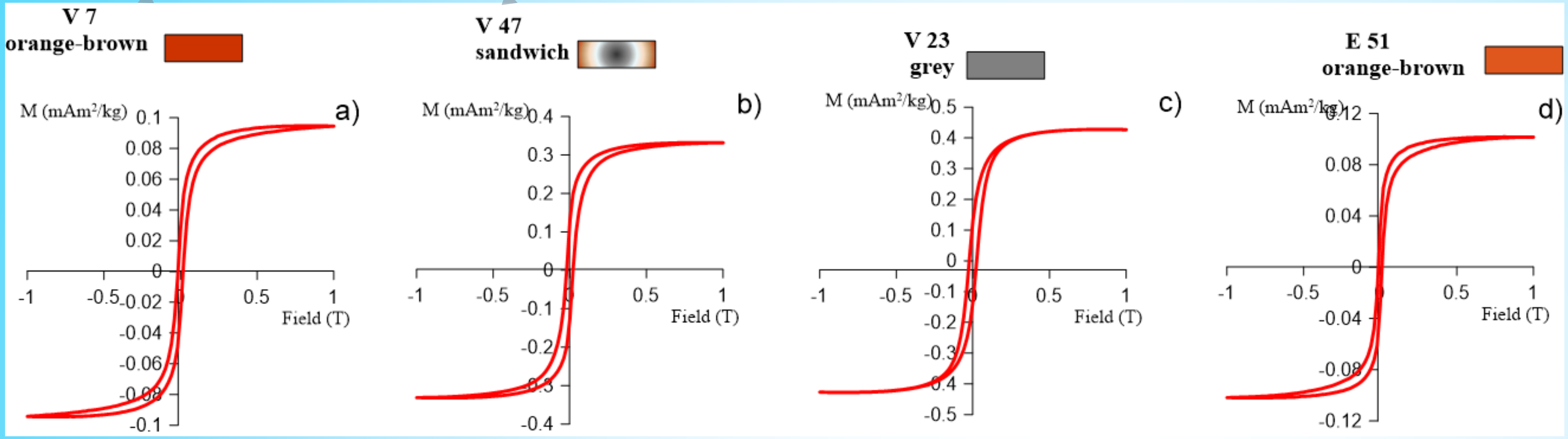
Magnetite – low Ti-titanomagnetite identified.

Pottery fragments from Pliska and Plovdiv *(source: Jordanova et al., 2019, Archaeol Anthropol Sci 11:3595-3612)*

10 – 11 c. AD

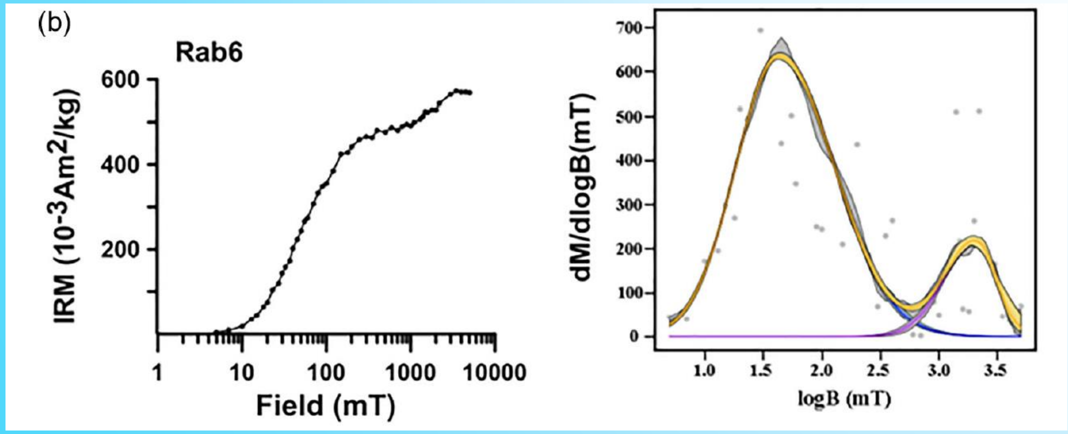
8 – 9 c. AD

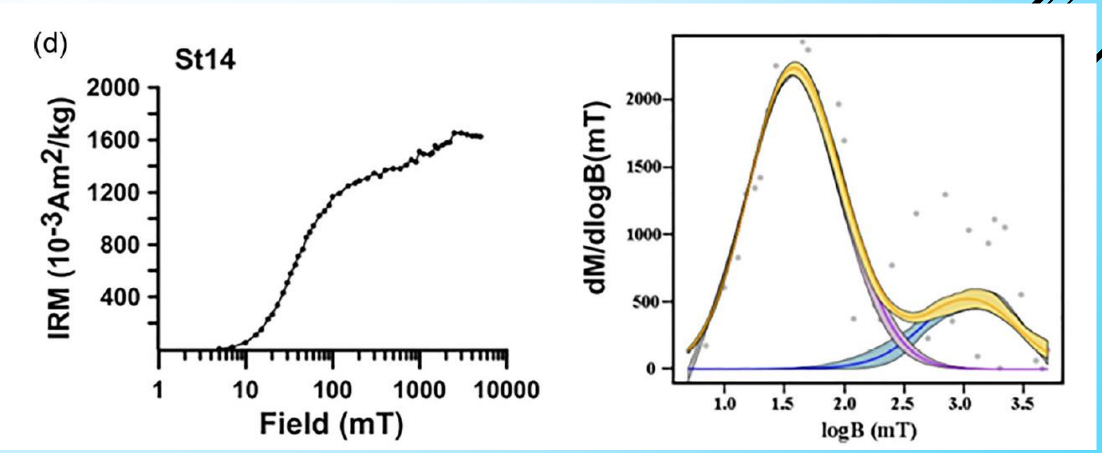
4 c. AD



- Magnetically soft mineral (magnetite – type) dominates
- BUT high-coercivity phase also frequently present – WWL hysteresis loops

Pottery fragments from Plovdiv *(source Lesigyarski et al., 2020. Geoarchaeology 35:287–309)*

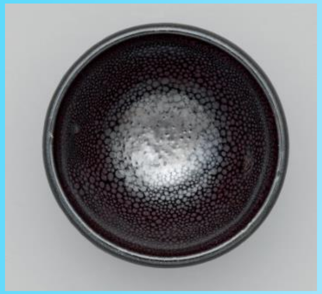




Finding of ε-Fe_2O_3 in ceramic pots

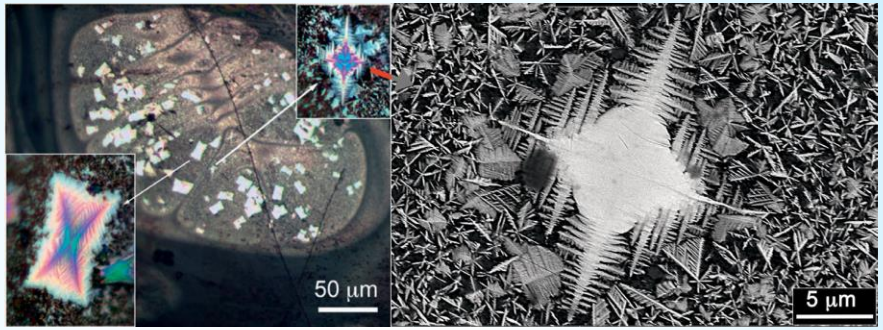
Glazed porcelain pots from China

Sciau et al., 2019, Technè [En ligne], 47 | 2019, mis en ligne le 01 juin 2020, consulté le 17 mars 2022. URL : http://journals.openedition.org/techne/1619 ; DOI : https://doi.org/10.4000/ techne.1619

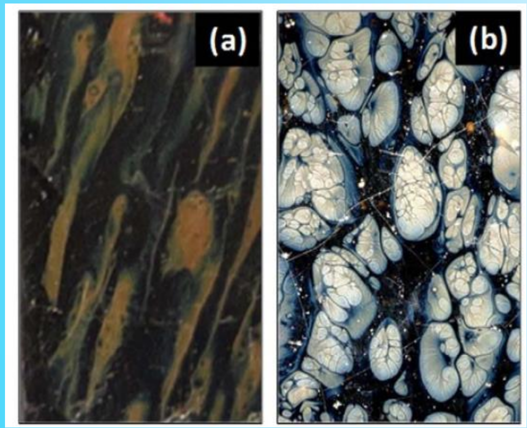


12th c. AD

17th c. AD

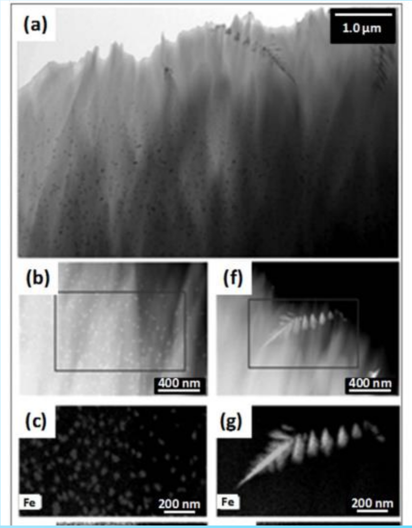


black-glazed Jian (Tenmoku) wares - Dejoie et al., 2014. *SCIENTIFIC REPORTS | 4 : 4941 | DOI: 10.1038/srep04941*



Optical microscopy – surface pattern of two samples

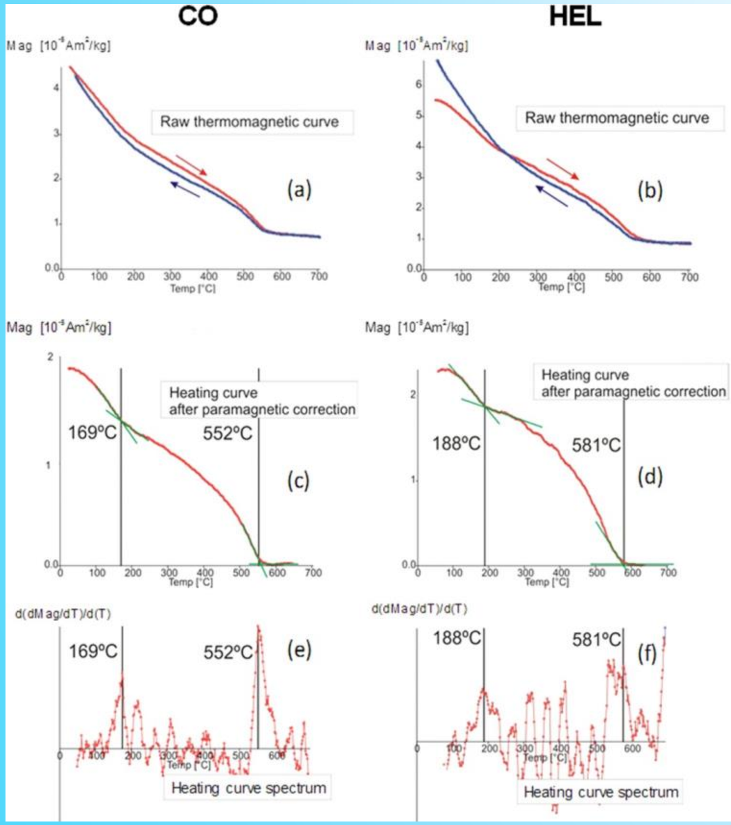
- the iron oxide crystallites are precipitated in the molten glaze during the cooling phase
- Two types of crystals were found - star shape and dendritic shape.
- EDX analyses revealed that Fe is the only cationic element present in these crystals
- identified iron oxide crystallites in brown strip (a) as a mixture of α-Fe_2O_3 (hematite) and the metastable ε-Fe_2O_3 phases of nm-size.
- the crystallites responsible to the "oil spot" (b) appearance are mainly ε-Fe_2O_3 of larger µm-size
-

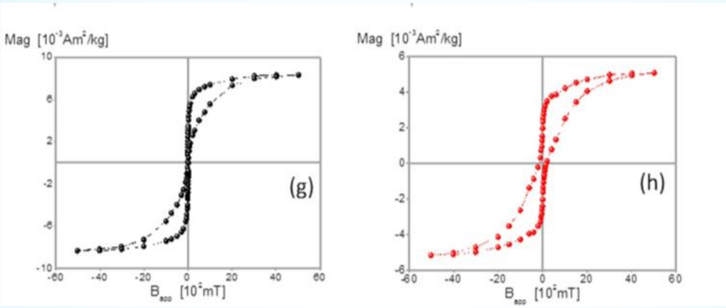


Magnetic properties of archaeological materials, containing ε-Fe_2O_3

Lopez-Sanchez et al., 2017, Geochem. Geophys. Geosyst.,18, 2646–2656

Sample CO - baked clay block used in the construction of a medieval kiln from Cordoba (Spain)
Sample HEL - modern brick (1906 AD) from Helsinki (Finland)



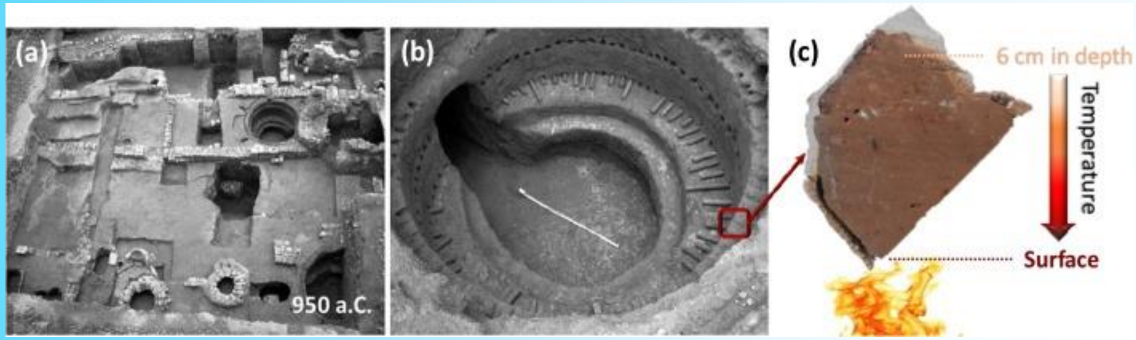


ε-Fe_2O_3
- Very high coercivity
- low Tc
- thermally stable

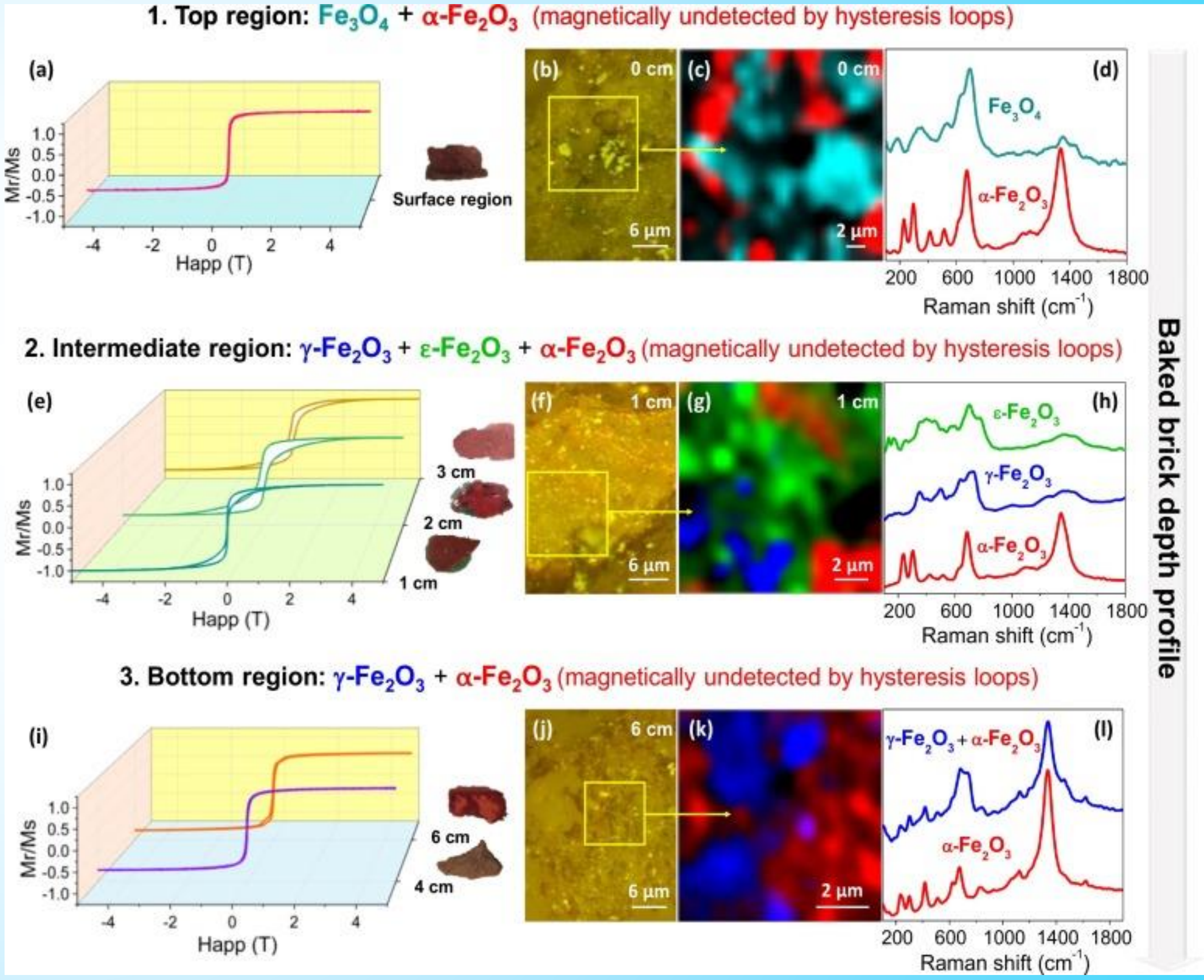
The widespread occurrence of hematite has been found in both samples, but due to its lower saturation magnetization it does not make a major contribution to the bulk magnetic properties. These are dominated by the presence of ε-Fe_2O_3 and maghemite in the baked clay (CO) and ε-Fe_2O_3 and either maghemite or magnetite in the brick (HEL).

Lopez-Sanchez et al., 2020, Physics of the Earth and Planetary Interiors, 307, 106554

Islamic pottery complex from Spain

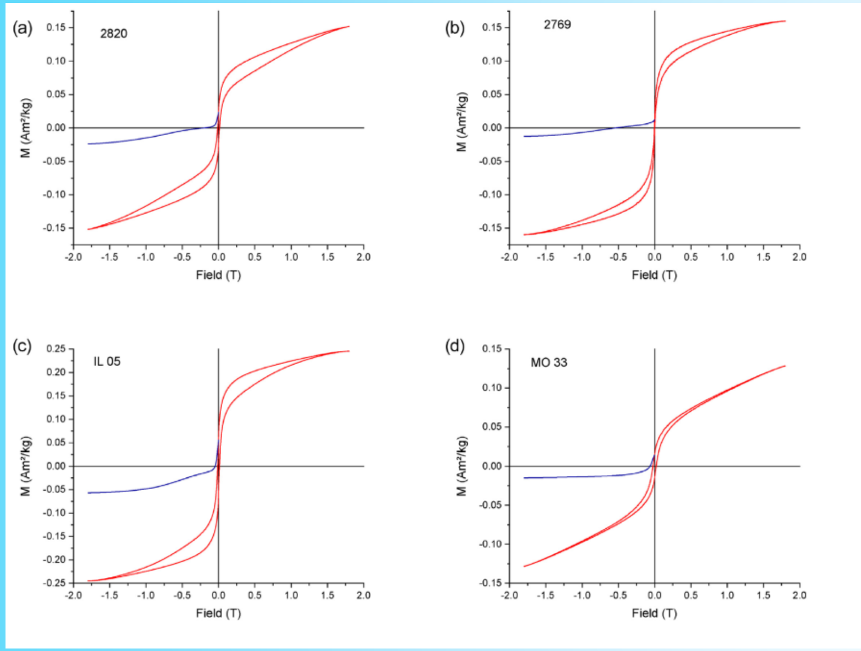


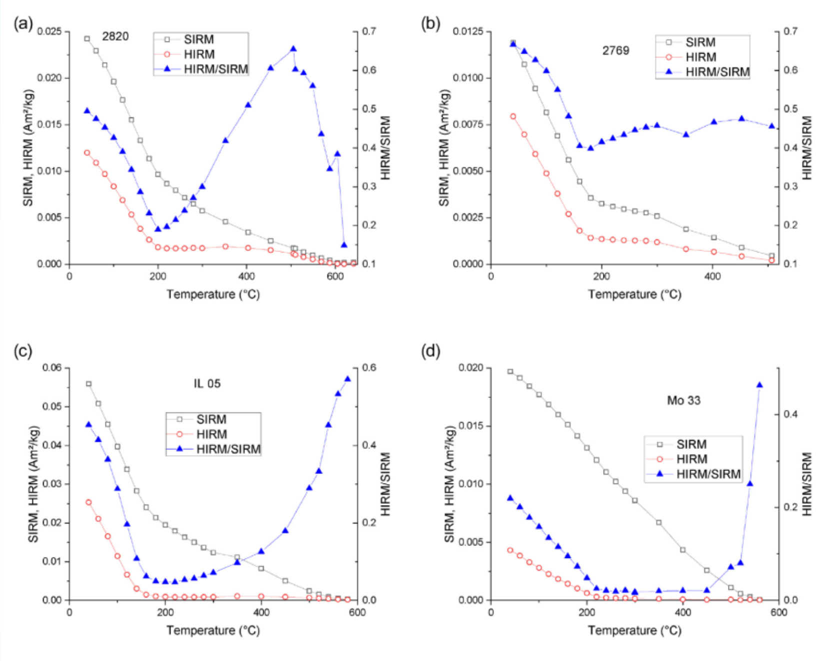
- The temperatures in the kiln probably reached 1200 °C.
- formation of Fe_3O_4 and α-Fe_2O_3/ γ-, ε-, and α-Fe_2O_3/ γ- and α-Fe_2O_3 in the top/intermediate/ bottom region.
- Maximum ε-Fe_2O_3 signature is detected at 2 cm in-depth in the specific case studied.



Bricks and fired clay from Neolithic combustion structures from Bulgaria and Russia

Kosterov et al., 2021. Geophys. J. Int. 224, 1256–1271





Magnetic minerals detected:

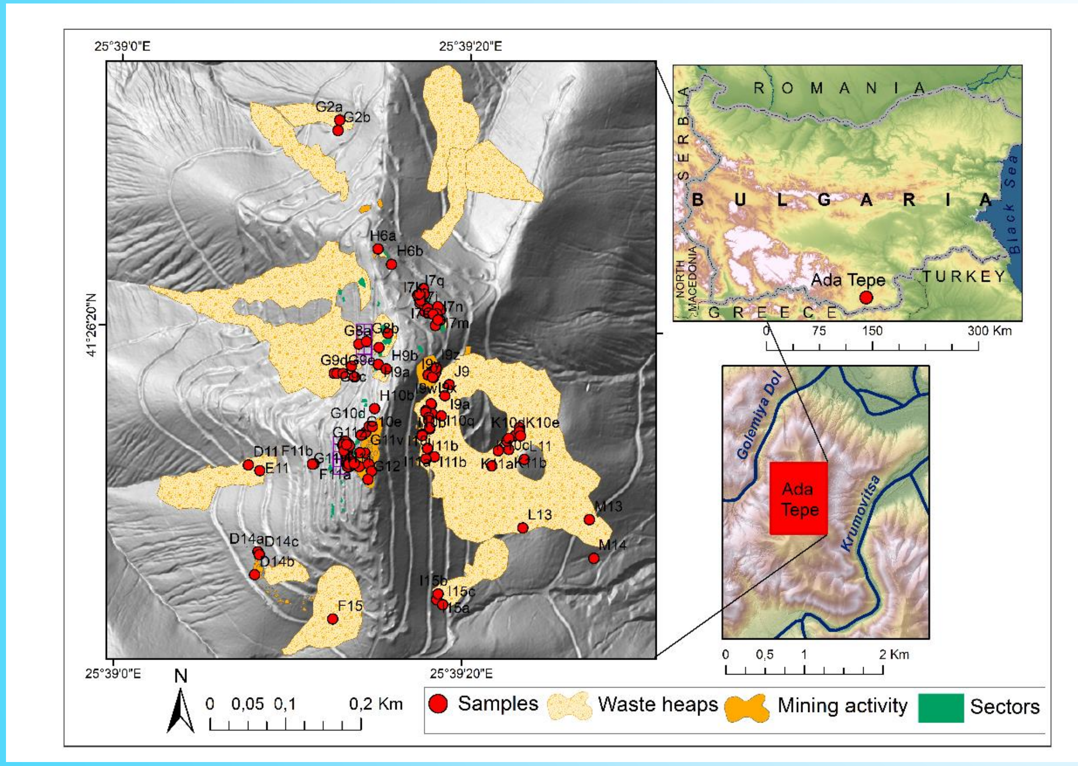
- magnetically soft, having room-temperature coercivity below 50 mT,
- two magnetically hard phases coercivities in the Tesla range.
- These two phases have very different unblocking temperatures:

1) 120–200◦C - ε-Fe_2O_3 with substitutions
2) 500–640◦C – fine-grained/substituted hematite

A CASE STUDY: MINERAL MAGNETISM APPLIED TO STUDY ANCIENT GOLD-MINING SITE

Jordanova et al., 2020, Geochemistry, Geophysics, Geosystems, 21, e2020GC009374.
https://doi.org/10.1029/2020GC009374

Late Bronze Age open-pit gold mine at Ada Tepe - the oldest known open pit gold mine in Europe

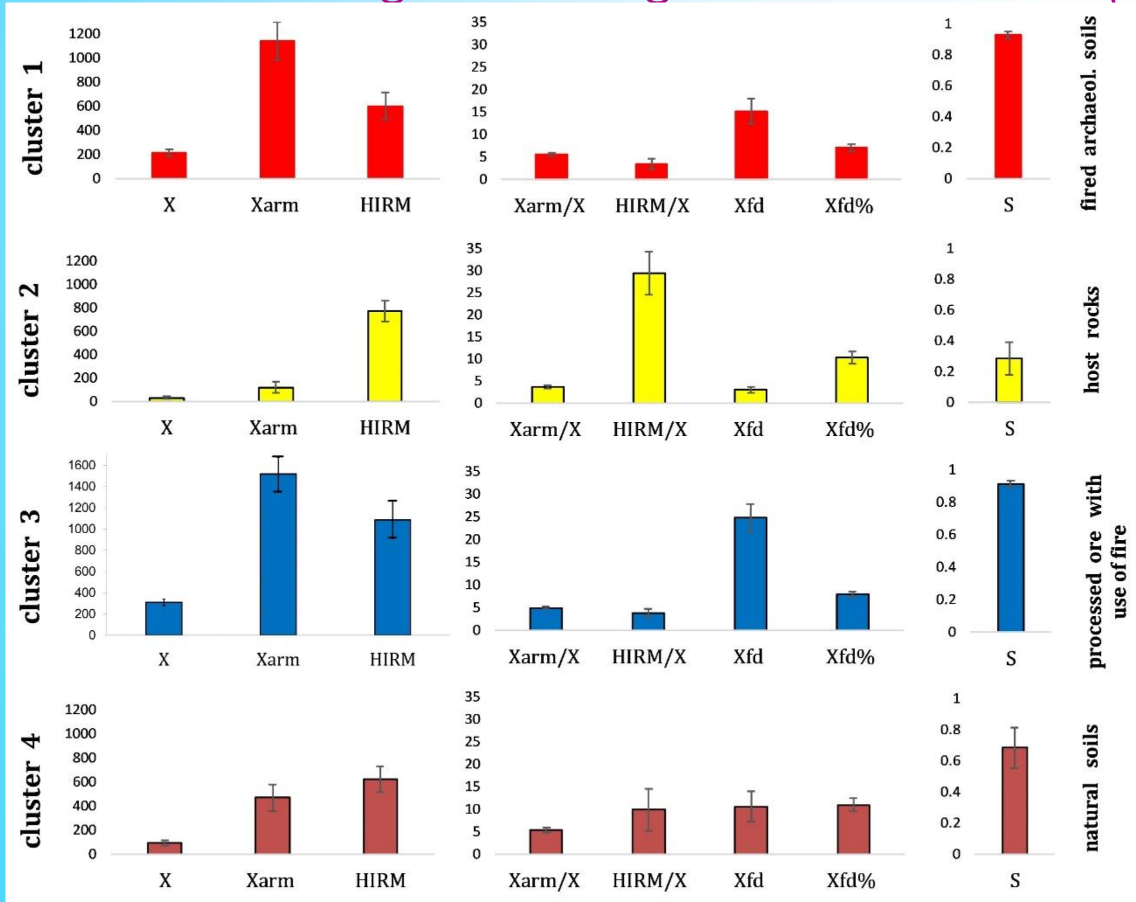


- ☺ gold mineralization is closely related to iron oxides/ hydroxides
- ☺ The waste material from the ancient gold mining was stored by the ancient miners in numerous rock heaps spread at a large area across the hill
- ☺ use of fire-setting in the ancient ore mining
- ☺ 177 loose samples are taken from different archaeological structures (waste heaps, places connected with the primary mining activities, ore-preparing working places, mounds, cultural layers and destructions from houses from the settlement areas
- ☺ extended set of mineral magnetic measurements applied

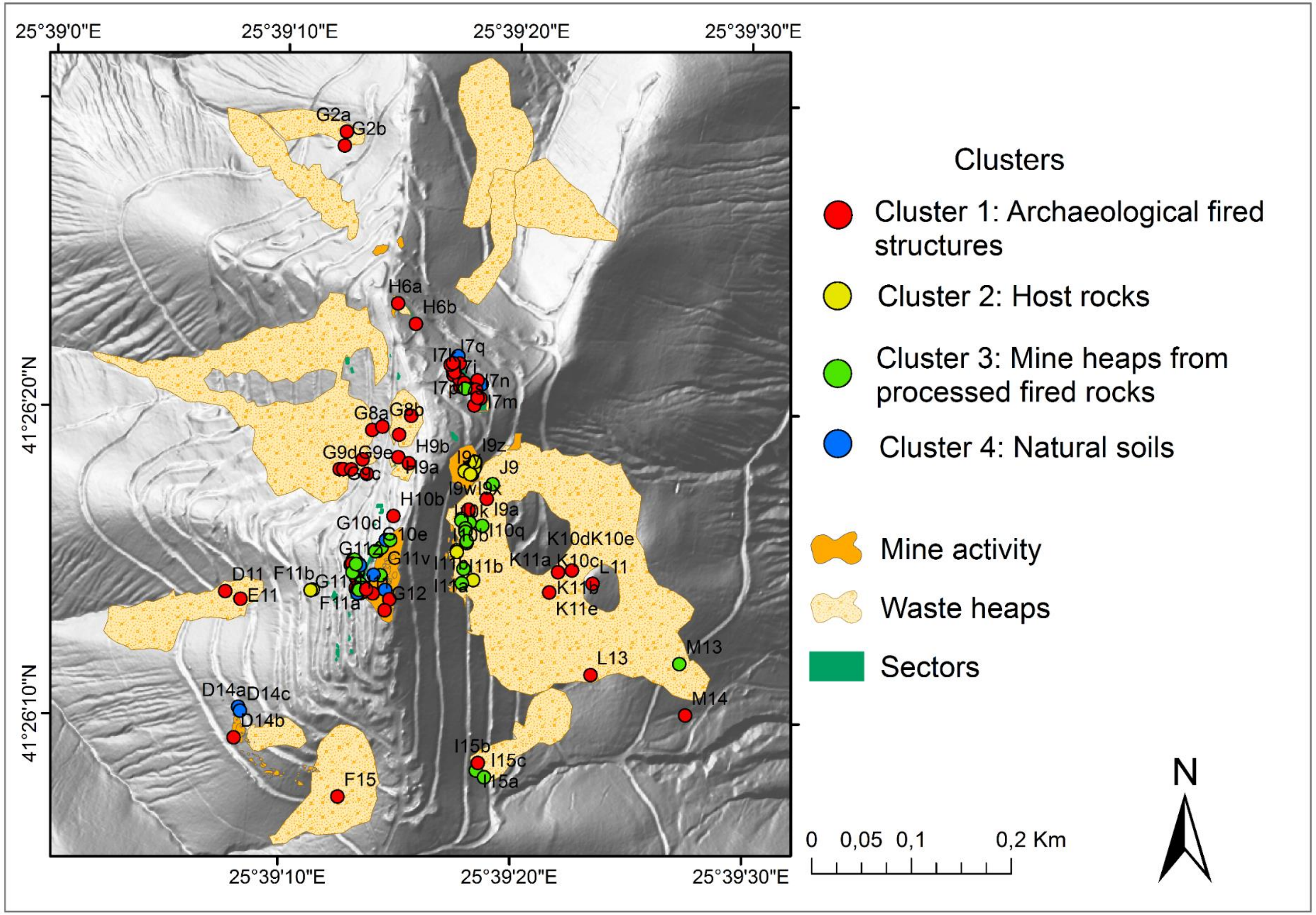
Magnetic parameters: χ, χfd%, ARM, IRM, bi-parametric ratios: $\chi_{ARM}/\chi fd$, χ_{ARM}/IRM, IRM/χ
Magnetic mineral identification

Factor analysis of the dataset – 4 clusters

Cluster #1: magnetite/maghemite and hematite
Cluster #2: goethite, hematite, magnetite/maghemite (minor amount)
Cluster #3: magnetite, pyrrhotite, hematite
Cluster #4: magnetite/maghemite, hematite, (?pyrrhotite), goethite (rare



Cluster #1—archeological fired structures
Cluster #2—host rocks
Cluster #3—mine heaps from processed fired rocks
Cluster #4—natural soils



The combination of the mineral magnetic approach with the stratigraphic and archaeological information allows deriving much more detailed and specific conclusions related to the overall organization and characteristics of the technological chain for the exploitation of the ore deposit during the Late Bronze age.

PART 6

MAGNETIC SUSCEPTIBILITY METHOD for evaluation of maximum firing temperature of archaeological pottery fragments – methodology, advantages and drawbacks

DETERMINATION OF ANCIENT FIRING TEMPERATURE – main principles

T_{max}

T_{max}

experimental firing of supposed raw clay

re-firing ancient pottery fragments

EQUIVALENT FIRING TEMPERATURE (EFT)

$T_{max} = EFT$

☝ **only when** identical firing conditions are used

After Daszkiewicz and Maritan, 2016

DETERMINATION OF Equivalent Firing Temperature

Static methods

experimental firings of samples made from a similar body

Dynamic methods

re-firing fragments of the original sherds and observing changes in composition and properties

Magnetic susceptibility method for determination of ancient firing temperatures

Developed by *Rasmussen et al., 2012, Journal of Archaeological Science 39, 1705-1716*

BASIC PRESUMPTIONS OF THE METHOD

1. magnetic susceptibility change upon heating is a function of:
   - minerals transformation temperatures/thresholds
   - grain size of newly created magnetic minerals

2. when ceramic vessel is cooled from its maximum firing temperature, the high temperature mineral assemblage produced will be preserved over archaeological time.

3. the maximum firing temperature can be reconstructed from the curve of the magnetic susceptibility as a function of re-firing temperature.

"original firing temperature" (To) - the temperature at which a ceramic product was fired by the potter who made it.

"re-firing temperature" (Tr) - the temperature at which a previously fired product was fired in the laboratory.

- If **re-firing** is carried out using **the same conditions as the original firing**, then during the course of re-firing at a temperature below the original firing temperature (To) no physicochemical changes should take place in the re-fired ceramic material
- phases "frozen" in the ceramic fabric at the To will not change until the firing process, interrupted at the To, is resumed
- Exceeding the original firing temperature (Tr>To) during the course of re-firing results in the resumption of thermal processes in the initial clay composition
- the temperature at which changes occur also depends on firing atmosphere and time, the result of re-firing analysis is referred to as **the equivalent original firing temperature Teq**

ORIGINAL METHOD DESCRIPTION

SAMPLE

- pottery sherd selected
- dried at 120ºC for 24h
- cooled

INI measurements

- Weight (g) (10 mg – 5 g)
- Magnetic susceptibility (k) – kappabridge/meter
- 4 single K measurements - averaged
- Empty holder signal subtracted

LAB RE-HEATING

- Heating in a muffle furnace with good accuracy of T-control
- First heating T = 200ºC for 24 h, cooling down to room T
- Measurements of K
- Temperature step is set to 20ºC up to 1000ºC
- Soaking time – progressively decreasing with increase in T – at 1000ºC – 30 min
- Measurements of K after each heating step

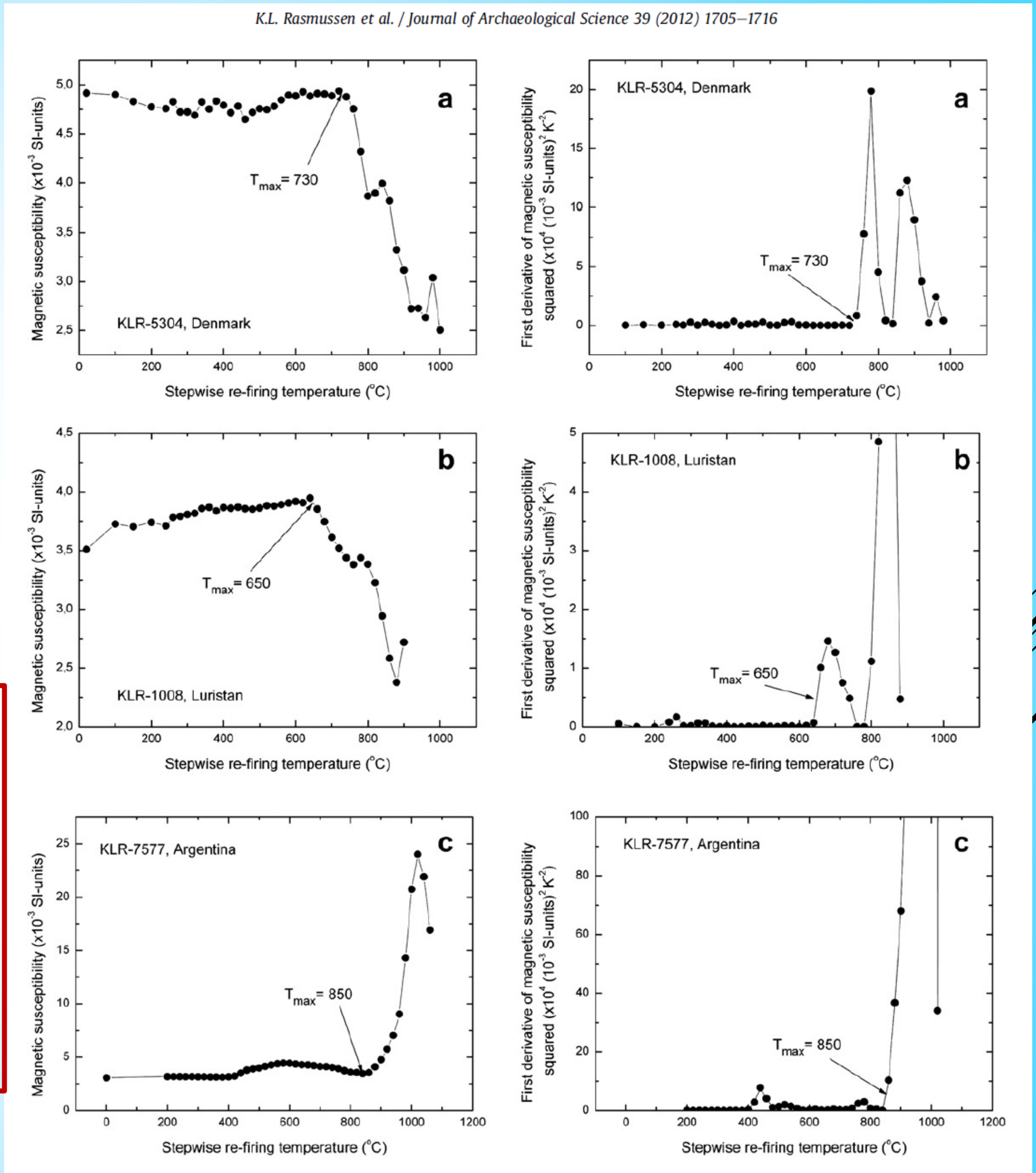
DATA PROCESSING

1. Construction of K-T graphs
2. calculation of the first derivative of K with T
3. plotting K(T) and $(dK/dT)^2$

__Tmax__ is defined as the temperature of the sudden discontinuity in K(T) and (dK/dT)²

➪ The method is validated through experimental firing and subsequent re-firing of clay samples

➪ uncertainty of the method is determined as a square sum deviation of the fired and the experimentally determined firing temperatures and is estimated to be **±25.8 °C.**



CONSTRAINTS OF THE METHOD

Laboratory re-firing is typically conducted in air (oxidizing conditions)

For ceramics which were originally fired under different conditions (reducing or partial oxidizing atmosphere), the Teq value will be affected by this change in atmosphere between the original firing and re-firing.

Fragments of gray pottery (originally fired in a reducing atmosphere), showed Teq values *lower* than those fired in air with a maximum of 70°C *(Daszkiewicz and Maritan, 2016, The Oxford Handbook of Archaeological Ceramic Analysis)*

Archaeological pottery fragments may be suffered alteration processes during burial.

Temperature gradient in a pottery kiln is of the order of ±50°C.
→ Teq determination with the same accuracy is acceptable.

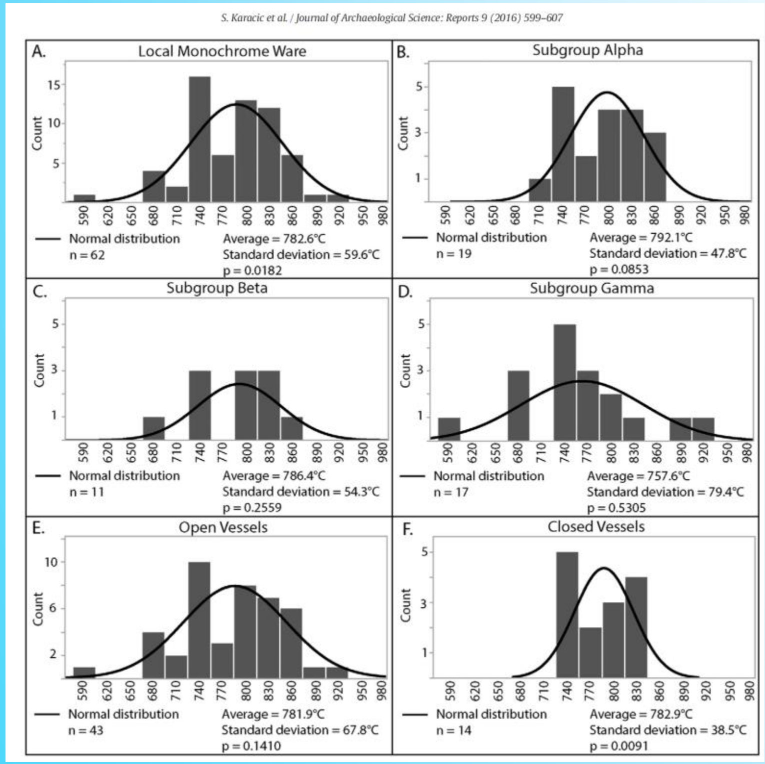
Examples of case studies of application of Tmax determined by magnetic susceptibility

POTTERY

INSIGHTS INTO POTTERY PRODUCTION

1. Bronze Age pottery from Turkey *(Karacic et al., 2016, Journal of Archaeological Science: Reports 9, 599–607)*

Samples collection: 62 Sherds from the LB IIA level at Tarsus-Gözlükule, 3 sub-groups

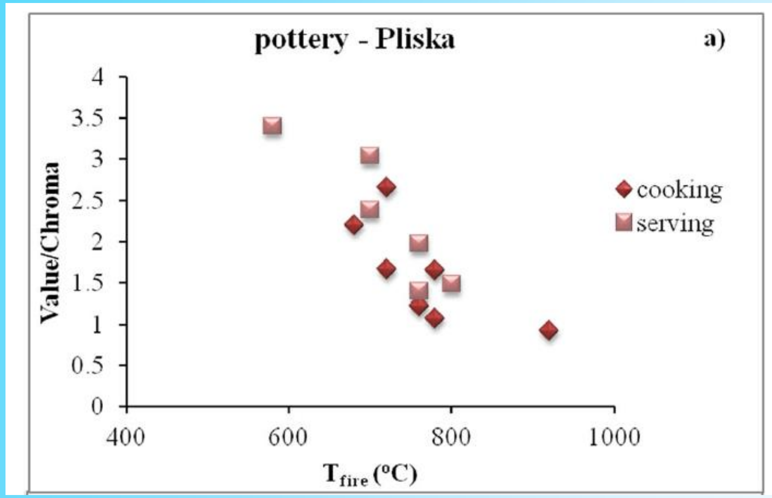


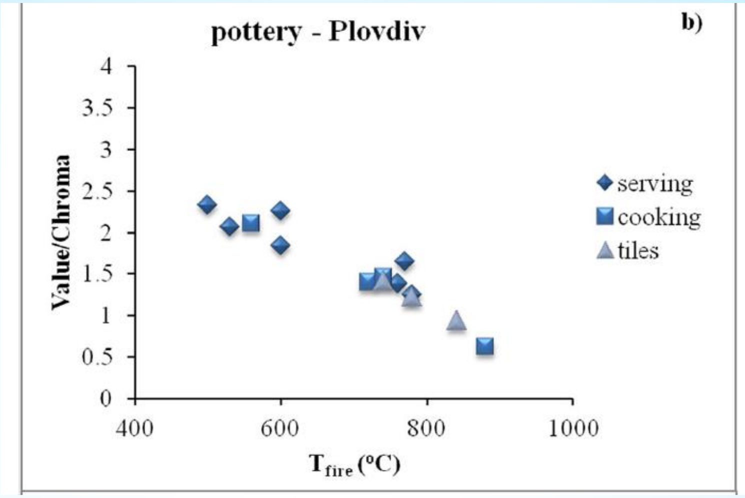
Tmax determined using magnetic susceptibility method
Data presented as histograms for each group
Statistical treatment (average, st.dev.)

? bi-modal distribution of Tmax : 1) 740 °C and 2) 800 °C to 830 °C.

Conclusion:
the potters consistently achieved two different maximum firing temperatures:
→ the pottery workshops used two different kilns
→ the potters may have employed two different types of fuel

2. Pottery from Pliska and Plovdiv (Bulgaria) *(Jordanova et al., 2019, Archaeol Anthropol Sci, 11, 3595–3612)*





Color measurements
Magnetic measurements

magnetic parameters could be regarded as linked to the color saturation of the burnt clay

- linear relationship between the estimated maximum firing temperature, and the value/chroma ratio found

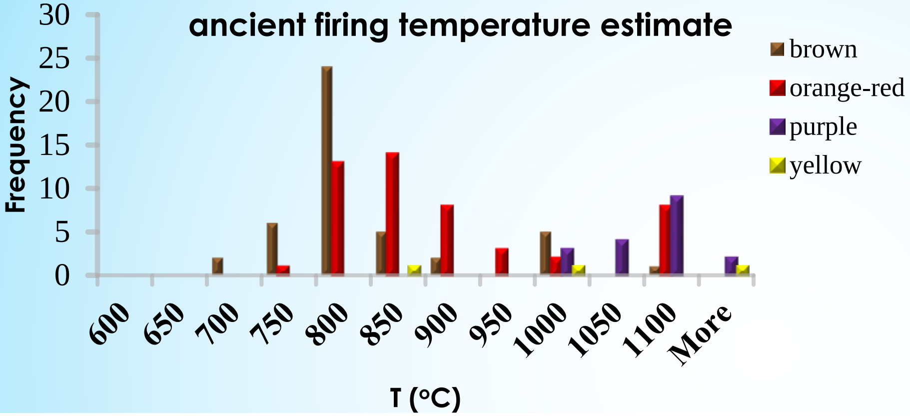
- "chroma" generally reflects the amount of the secondary Fe oxides (e.g., produced during heating) in burnt clay and heated soil
- "value" could be related to the "amount of black".

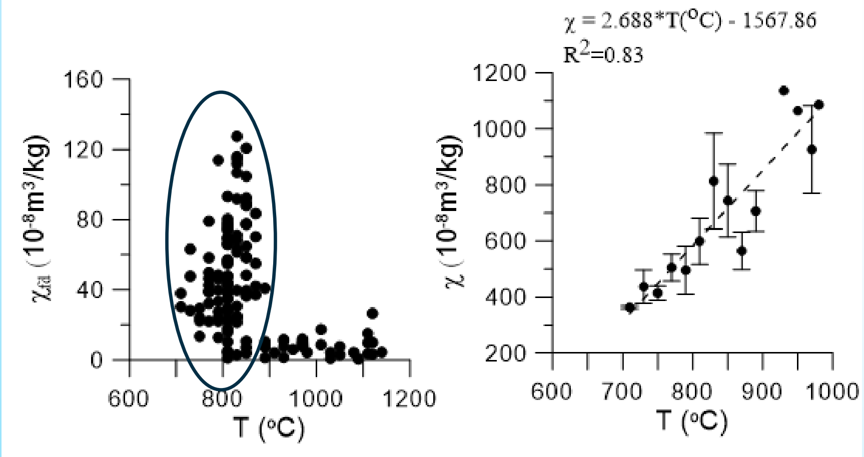
Therefore, the ratio value/chroma may be considered as an index of the degree of conversion of magnetite into hematite during progressive heating to higher temperatures.

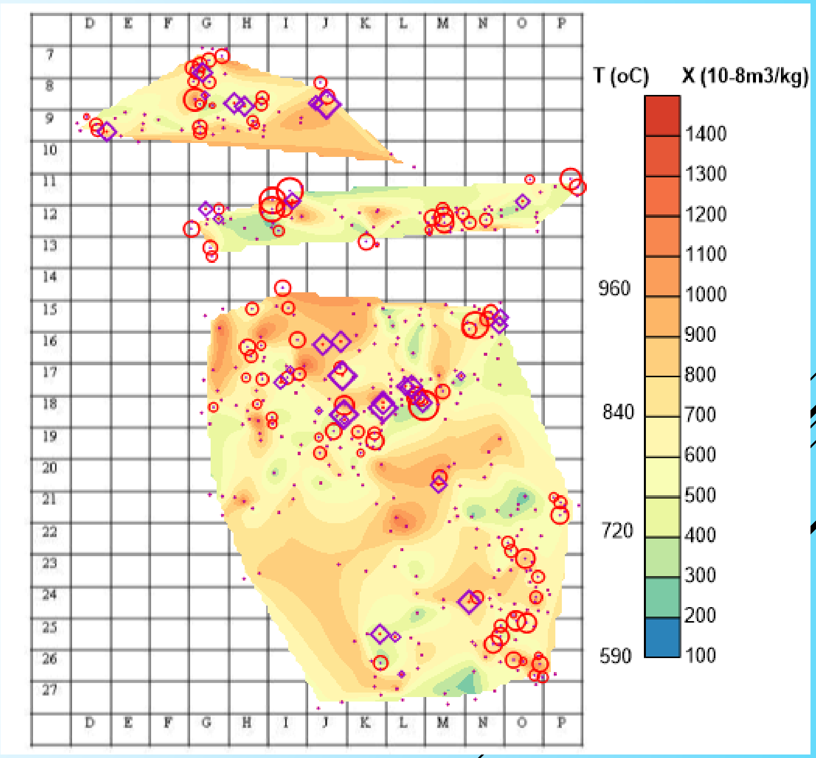
- parameters of the linear regression are different for pottery samples from different sites – the method could be applied for clay source discrimination

BURNED NEOLITHIC SETTLEMENT

Neolithic site Mursalevo-Deveboaz (Bulgaria) *(Jordanova et al., 2018, Journal of Geophysical Research: Solid Earth, 123 (4), 2522–2538)*







Reconstructed fire intensity across the settlement using Tmax estimates

- **SP- fraction (through χ_{fd}) separates samples according to T_{fire}**
- χ_{fd} threshold at 10 x$10^{-8}m^3/kg$
- **for samples with χ_{fd} > 10 x$10^{-8}m^3/kg$ - linear relationship between T_{fire} and magnetic susceptibility**

SUMMARY

- Fire significantly affects all Earth's compartments, especially soil and ancient settlements
- Iron-containing minerals is soil/clay undergo critical thermal transformations upon heating/burning
- Environmental magnetic techniques provide sensitive tools for monitoring those changes
- Characteristic transformation temperatures of iron (oxy)hydroxides serve as identification tools in rock-magnetism
- Archaeological finds of burnt clay store important information on the firing conditions and processes which can be recovered by rock-magnetic measurements
- Magnetic enhancement of fired clay materials is due to the presence of: magnetite, maghemite, hematite of varying grain size from SP to PSD-MD
- Firing atmosphere is one of the most important environmental parameters which influences magnetic properties of fired clay materials
- Magnetic susceptibility method for retrieving the maximum firing temperature of archaeological ceramics and burnt clay provides sensitive estimate of the ancient firing conditions

THANK YOU FOR YOUR ATTENTION!!!