NEOFORMED MINERAL PHASES DURING CLAY CERAMIC FIRING

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ABSTRACT

Ceramic clays are one of the most complicated ceramic systems because of the very complex relationship between the behavior of minerals during the ceramic processing and the transformations during heating. A major challenge is to predict the phase transfomations in clay ceramics. The aims are to establish reference data of ceramics products that can be formed based on the mineralogical composition of the local raw materials. These data, in turn, can be compared with the archaeological ceramics in order to study their origins.

The mineralogical compositions and transformations during the firing (550 to 1100ºC under oxidizing conditions) of seven clayey materials sampled from the main clay deposits of Northern Morocco were evaluated by X-ray powder diffraction. Two groups of clays were evidenced according to the type of neoformed high-temperature minerals: non-calcareous clays and calcareous clays. For the non-calcareous raw materials, spinel is produced at 950°C. Cristobalite and mullite were formed above 1000ºC from clays that contain illite, kaolinite and chlorite. In clays containing vermiculite and high amount of chlorite, hematite was formed from 950°C. Firing of calcareous clays at temperatures > 950ºC yielded Ca-silicates (diopside, gehlenite and wollastonite), spinel, cristobalite, hematite and feldspars. Mullite may also form in the calcareous clay products, when the carbonates content exceeds 10%.

Keywords: Clay; Raw materials; Ceramic; X-ray powder diffraction; Neoformation

INTRODUCTION

Clay minerals undergo a complex path of thermal transformations during heating (Henn *et al.*, 2007; Kam *et al.*, 2009), which determine the final properties of the ceramic products. A major challenge is to predict the phase transformations in fired ceramic clays, since complex relationships occur between the structural characteristics of the fired products and the chemical properties of the fired ceramics.

Upon firing, the minerals in the fired ceramic clays undergo chemical and structural modifications deeply transforming the original clayey materials. The high temperature, low-pressure mineral transformations are mainly influenced by the chemical and mineralogical compositions of the raw materials, the maximum heating temperature, heating rate, duration of firing and kiln redox atmosphere (Lin, 2007; Khalfaoui and Hajjaji, 2009; Pardo *et al.*, 2011).

Fired ceramic clays have a complex mineralogical composition, which makes the study of neomineralizations and the disappearance of mineral phases present in the raw material rather difficult (Jordán *et al.*, 2001). It is difficult to maintain the stability of these crystalline structures, once they cross their stability limits, partially decompose and then simultaneously form other phases (Jordán *et al.*, 1999).

The present work focuses on the mineral transformations with increasing temperature for 7 clays of widely varying mineralogies from northern Morocco to assess their suitability for the production of ceramics. The main aim was to study the mineral transformations of natural clays with increasing temperature and to establish reference groups for local ceramic industry based on raw-material composition and high-temperature mineralogy.

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MATERIALS AND METHODS

The studied clays belong to three clay deposits of Morocco which can be used in ceramic pastes. The clays came from Northern Morocco at Meknes, Tangier and Tetouan regions. The geological background of the mineralogical, textural, and geotechnical compositions of those clays were previously described by El Ouahabi *et al.* (2014b).

Seven samples have been selected based on the mineralogical characterization of 52 clay samples from the main clay deposits of Northern Morocco (El Ouahabi *et al*., 2014b). The samples representing the observed compositional variability were selected for firing experiments to study the mineral evolution during ceramic firing process. The main compositional criteria were related to the presence/absence of carbonates, their composition (calcite or dolomite) and abundance, the type of phyllosilicates (clay minerals) and their relative proportions, and the presence/absence of Fe-rich minerals (hematite). Following their mineralogical composition, we identified two groups of clays, rich in carbonates (CC) and non-calcareous (NC) clays. The presence of carbonates, as well as their type (calcite or dolomite) affects the firing behavior and crystallization of minerals at high temperatures (Tite and Maniatis, 1975; Czímerová *et al.*, 2006; Demir, 2008).

The studied clays were composed mostly of quartz, illite, kaolinite and variable amounts of calcite, chlorite, vermiculite, smectite, feldspars, hematite and muscovite (El Ouahabi *et al.*, 2014b). The chemical composition (Table 1) of the selected clays consist of SiO_2 (35 - 51%), Al_2O_3 (14 – 34%), CaO (0 – 19%), Fe_2O_3 (0 – 15%), and small amount of MgO and K_2O(El Ouahabi *et al.*, 2014a).

Seven clay samples were oven dried at 35°C for 48 h. Dried clay was ground and sieved through 20 mm to simulate industrial pressing conditions. Each clay sample was wetted in

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order to achieve the proper plasticity for molding. The samples obtained with these shaping techniques were: 4 cm long, 2 cm wide and 2 cm thick. The drying was done in shaded and ventilated room. The dried samples (24 h at shaded room plus 12 h at 105°C in oven) were kiln-fired at different temperatures (550, 950, 1000 and 1100°C) for 1h at rate of 10°C/min. The analysis of mineralogical phases of the fired samples was carried out by X-ray diffraction (XRD), using Bruker D8-Advance diffractometer with CuKα radiations (Department of Geology, University of Liege, Belgium) on powdered bulk sediment following the procedure for clay analysis, as described by Trindade *et al.* (2009). The X-ray powder patterns were treated by the DIFFRACplus EVA software to remove the background noise and to calculate profile parameters such as line positions and peak intensities. The estimation of mineralogical composition is based on the maximum count rate at the top of each characteristic peak d(001).

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The chemical composition of selected elements (Si, Al, Fe, Ca, Mn, Mg, Na, K, Ti, P and S) was measured as oxides on 2 g of dried and homogenized powder of clayey samples using a Bruker S8 Tiger wavelength-dispersive X-Ray Fluorescence (WD-XRF) spectrometer equipped with a Rh anticathode (Department of Ecology and Environmental Sciences, Umeå University, Sweden). Reproducibilites are above 99% except for S (89%) and P (97%). More details about the method and the calibration can be found in De Vleeschouwer *et al.*, (2011). The same powdered samples were heated to 1000˚C for 2 h to determine the Loss On Ignition (L.O.I).

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RESULTS AND DISCUSSION

The clay ceramic industries are usually based on chemical data (XRF) to predict the neoformation of crystalline phases during firing. The implication of carbonates and non-calcareous clays in the formation of the glassy phase, mullite, and cristobalite is discussed by using $SiO_2/Al_2O_3/NaO_2+K_2O$ and $SiO_2/Al_2O_3/CaO$ equilibrium diagrams (Figure 1).

Due to the position of the representative points of the chemical compositions of original phases $SiO_2/Al_2O_3/NaO_2+K_2O$ diagram (Figure 1), mullite should be formed. Referring to literature data (Cultrone *et al.*, 2001; Khalfaoui and Hajjaji, 2009), mullite is derived from the aluminum content, related to the presence of clay minerals and micaceous-rich minerals.

In the $SiO_2/Al_2O_3/CaO$ equilibrium diagram (Levin *et al.*, 1964), non-calcareous materials produce high temperature phases such as mullite. In the calcareous clays the presence of CaO avoid the formation of the mullite. Decomposed clay minerals form, in combination with CaO, phases like gehlenite, anorthite, wollastonite, instead of mullite (Peters and Iberg, 1978; Czímerová *et al.*, 2006). For the silica-rich, material cristobalite phase was formed in carbonate-rich clays. Tridymite could also be observed as an intermediate phase before the formation of the cristobalite, depending on the relative proportions of the three components (SiO_2, Al_2O_3, CaO) and the temperature of firing.

The results (Figure 2 and 3a-b) and related discussion for mineralogical transformations as function of temperature are based on the two groups of raw materials defined above: (1) non-calcareous clays; (2) and carbonate rich clays. The mineral abbreviations used in this study are from Whitney and Evans (2010).

Overall, the first mineral transformations (Figures 2a-b and 3) observed with increasing temperature included the dehydroxylation of kaolinite before 550ºC, followed by other clay minerals (illite, chlorite, smectite, and vermiculite), which dehydroxylated close to 950ºC. Calcite and dolomite transformed into lime (CaO) and then reacted with other components to generate neoformed calcium minerals, such as gehlenite, diopside and wollastonite (Trindade *et al*., 2009). Generally, K-feldspars disappeared below 1000ºC, plagioclase seemed to persist up to 1100ºC, and quartz is preserved even at 1100ºC.

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Non-calcareous clays

Three non-calcareous clay samples (NC1, NC2 and NC3) were kaolinitic and illitic clays with high quartz content (Figure3 and 4a). Chlorite was only present in NC2 and NC3 in small amount. Smectite was present in NC1 (El Ouahabi *et al.*, 2014b). Small amount of hematite was observed. Plagioclase was another constituent, which was absent in NC3 clay.

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Relative to mineral transformations (Figures 3a, 4a, and 5) of NC1, kaolinite and illite/smectite disappeared at 550ºC and 950ºC, respectively. Plagioclase and muscovite disappeared close to 950°C and was replaced by alkali feldspars. Quartz and hematite were present throughout the entire temperature range. Hematite showed a slight increase, whereas quartz is reduced by a factor of 2 at the maximum firing temperature. Neoformed mullite and K-feldspar appeared at 950ºC and reached its maximum abundance at 1100ºC.

Despite their variable starting composition, NC2 and NC3 showed similar neoformed minerals. Mineral transformations with firing included the loss of all phyllosilicates from 950 to 1000ºC, muscovite at 950°C, and plagioclase close to 1100ºC. Quartz and hematite remained up to 1100ºC, with their maximum abundance at maximum fired temperature. Spinel formed at 950°C, followed by mullite and cristobalite at 1000°C. Mullite and cristobalite were more abundant at 1100ºC.

All the samples studied contain Mg-rich spinel, probably derived from the dehydroxylation of clay minerals rich in MgO, chlorite and smectite. Spinel was formed by the reaction: MgO + Al_2O_3 → $MgAl_2O_4$. Cristobalite and mullite are found in NC2 and CN3, due to phyllosilicates transformation, particularly illite (Cultrone *et al.*, 2001). According to their mineralogical composition, those clays contain ~20% of muscovite and illite, respectively (El Ouahabi *et al.*, 2014b). Cristobalite is probably produced by quartz transformation, as

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observed previously (e.g., Elert *et al.*, 2003). The major original mineral at high-temperature is quartz, which is the most abundant phase in all fired clay samples. Other original minerals accompanying quartz up to 1100ºC are hematite.

The neoformed mineralogy for non-calcareous clays was relatively simple, consisting of spinel, cristobalite, and mullite and K-feldspar. Mullite appeared at 1000ºC in quartz rich clays, and its abundance increased at higher temperatures (Figure 5). One could say that the quartz content (about 50%) in addition to phyllosilicates promote the formation of mullite. Cristobalite was identified only in the quartz-rich clays (NC2 and NC3) at 1000ºC. The neoformed K-feldspar observed after firing at high temperatures in NC1 clay is suggested to be a high-temperature phase which replaced illite/muscovite phase.

Firing below 950°C induced no significant mineralogical transformations and noeformations began from 950°C. Feldspars (K-feldspar and plagioclase) neoformed at 950°C, act as a flux that facilitate easy melting at firing. During clay firing especially, micaceous minerals especially change to mullite, K-feldspar and plagioclase (Cultrone *et al.*, 2001; Khalfaoui and Hajjaji, 2009).

Carbonate rich clays

Four carbonate rich clays (CC1-CC4) were kaolinitic and illitic clays (Figures 3b, 4b and 5), with a high quartz content. Chlorite is the major clay mineral phase in the CC1 sample, while it is found in trace amounts in the other samples. In CC3 sample, vermiculite is the principal clay mineral phase. Variable amounts of calcite were identified, whereas small amounts of dolomite, plagioclase and K-feldspar are present in these carbonate clays (El Ouahabi *et al.*, 2014a).

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For CC1, calcite, phyllosilicates were the first minerals to disappear at 950ºC. Plagioclase, dolomite and quartz were present throughout the temperature range, but the abundance of quartz and dolomite decreased at 1100ºC. The first minerals neoformed were gehlenite and diopside, which appeared at 950ºC, followed by spinel at 1000°C. The gehlenite content decreased at higher temperatures, and diopside and spinel were more abundant at 1100ºC. K-feldspar disappeared close to 950ºC, plagioclase seemed to persist up to 1100ºC, and increased in amount.

The mineralogical transformations, reported in figures 2b and 3b, indicate that when the temperature is increased to 950°C, $CaCO_3$ decomposes to CaO, phyllosilicates decompose and spinel type phases appear. CaO reacts with Si and Ca-silicates appear, such as gehlenite, diopside and wollastonite. As the temperature further increases, the gehlenite content decreases; this mineral seems to be a metastable neoformed phase.

The first mineralogical transformations of CC2 were the disappearance of calcite, phyllosilicates at 950ºC. Plagioclase, K-feldspar, dolomite and quartz were still abundant after firing at 1100ºC. Plagioclase and K-feldspar increased their abundance up to 1000°C. Gehlenite, diopside and hematite were first neoformed minerals identified at 950ºC, and their abundance was maximum at 1100ºC. Hematite resulted from the iron released during chlorite and illite decomposition. Spinel and cristobalite were present at 1000ºC; their maximum abundance was observed at 1100ºC. Mullite was the last phase neoformed at high temperature, close to 1100°C.

Relative to mineral transformations of CC3, kaolinite disappeared at 550ºC, whereas calcite and vermiculite were persisted up to 950ºC. Quartz was the only one present throughout the entire temperature range, with its abundance being very low at the maximum firing temperature<_e. Neoformed minerals were diversified; they included plagioclase, K-

feldspar, diopside, gehlenite and hematite. All neoformed minerals appeared at 950°C and were most abundant at 1100ºC, with an exception for hematite and gehlenite.

During firing of CC4, phyllosilicates disappeared at 950ºC and K-feldspar at 1000ºC. Plagioclase and quartz remained at the highest temperature of firing in very small amounts. Gehlenite, diopside, cristobalite and spinel formed at 950ºC, where they attained maximum abundance at 1000°C. Later, wollastonite is formed at 1100°C, with relatively high abundance. Diopside, cristobalite, gehlenite and spinel increase their abundance gradually.

The most significant mineralogical changes are observed in samples with carbonates, when fired at T > 800°C. Firing caused the decomposition of carbonates, clay minerals, and silicates and the formation of a melt phase rich in Si, Al, Ca, and K (Czímerová *et al.*, 2006). From this melt phase, neoformation and crystallization of several metastable phases occurred, continuously reacting with increasing temperature.

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All the calcareous clay samples contain gehlenite and diopside, which formed due to the presence of $CaCO_3$. In addition hematite, spinel, cristobalite and anorthite are formed. Wollastonite is neoformed only in CC4 at high temperature close to 1100°C. Melting starts just before 950°C when carbonates are present (Tite and Maniatis, 1975). Ca and Mg from carbonates may act as melting agents but they are reported to somehow limit the extent of vitrification at temperature above 1000°C (Cultrone *et al.*, 2001). On the other hand, the higher SiO_2 content in these samples provides a higher amount of potential silica-rich melt.

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Gehlenite starts to form between 550 and 950°C, when Mg is absent, by reaction between CaO from carbonates, Al_2O_3 and SiO_2 from the dehydroxylated phyllosilicates (Peters and Iberg, 1978). Diopside starts also to form between 550 and 950°C in all calcareous clays by reacting of Ca, Mg and SiO_2 from dolomite and quartz for CC1 and CC2; however Ca is

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probably supplied from calcite, Mg seem to come from vermiculite or chlorite for CC3 and CC4. In the case of wollastonite, these mineral stemed from reaction of CaO with SiO_2 at high temperature, its neoformation is marked mainly by a sharp decrease in quartz content (Figure 5). Wollastonite improves strength as well as water and heat resistances of ceramics (Azarov *et al.*, 1995).

Neoformed hematite resulted from dehydroxylation of Fe-rich clay such as vermiculite, in our case. Unfired clays with hematite, increased their amount in heated samples with rising temperature. This suggests that ferric oxide may be formed by the decomposition of clay minerals with non-negligible amounts of iron (Murad and Wagner, 1998). At higher temperature (1100°C) phyllosilicates have already disappeared in all samples, being transformed into spinel for most of clays, and further into mullite for CC2. Thus, the spinel phase essentially originated from decomposed chlorite, i.e. the principal Mg-bearing mineral. Spinel is absent in clays that do not contain chlorite (CC3). Between 550 and 950°C, the appearance of the reflections at 3.2 Å, 3.18 Å and 4.4 Å for CC3 indicated the formation of calcium aluminium silicate phase, anorthite ($CaAl_2Si_2O_8$).

The most significant difference between the calcareous fired clays is the appearance of mullite and hematite only in CC2 from 1000 and 550°C, respectively. Mullite appeared at high temperature, which could be related to the presence of enough content of illite/muscovite. At 1100°C, when illite and muscovite have already disappeared. They react with quartz, being transformed into mullite plus a melt (Cultrone *et al.*, 2001). During firing, Fe is generally responsible for the formation of mullite (Cuevas *et al.*, 2009). Plagioclase decreases slowly and K-feldspar decreased at 1000°C. Feldspars (especially alkali feldspars) are fluxes, so they may be neoformed during firing, as demonstrated by their increase from 1000ºC, which can be attributed to the formation of mullite (Czímerová *et al.*, 2006).

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Illite/muscovite undergoes a change to mullite and K-feldspar, plus a melt, according to the following reaction (Elert *et al.*, 2003):

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$3KAl_2(Si_3Al)O_{10}(OH)_2$ (illite/muscovite) + $2SiO_2$ → $3KAlSi_3O_8$ (K-feldspar) + $Al_6Si_2O_{13}$ (mullite) + $3H_2O$ + melt

In the clays with small amount of carbonates (< 10%), CC1 and CC4 samples, the fired clays consisted mainly of quartz, diopside, cristobalite, spinel, gehlenite and wollastonite. Cristobalite appeared in clay with high amount of quartz. We note the absence of the mullite phase in those samples: small quantities of carbonates (< 10%) clearly inhibit the formation of mullite and form instead Ca rich aluminosilicates. Mullite was formed in carbonate rich clays when the carbonates exceed 10%, with sufficient quantity of Al (associated with the abundance of plagioclase and illite/muscovite). With a small amount of Al, anorthite is formed instead of mullite.

The results can support provenance study issues, in developing a compositional databank and establishing reference groups of ancient clay from Moroccan sites. Such study could help to answers some archaeologist's questions concerning places and regions of origin, to determine technique for the production of artefacts, and to interpret cultural influences. Therefore, with the determination of the chemical and mineralogical composition of ceramic shards it will be possible to related it to a specific clays source and conditions of production, namely the firing temperature.

CONCLUSION

Clay ceramics undergo significant mineralogical modifications upon firing. Different types of clay-rich materials formed distinct associations of high-temperature phases during firing. The main assemblage of fired products is controlled by the initial mineralogical composition, in particular the carbonates content.

Firing non-calcareous raw materials produced spinel between 550 and 950°C. Cristobalite and mullite was formed above 1000ºC from clays that contain illite, kaolinite and chlorite. In clays containing vermiculite and high amount of chlorite, hematite was formed between 550 and 950°C.

In calcareous clays, Ca-silicates (diopside, gehlenite and wallostonite) were accompanied by spinel, cristobalite, mullite, hematite and feldspars. The presence of small amount of carbonates inhibited mullite formation, and instead Ca-silicates (gehlenite and wallostonite) were formed. When the carbonates exceeded 10%, mullite was formed, but its formation depends on the quantity of Al. when the Al content is too low to form mullite, then a small amount of anorthite is formed instead of mullite.

The mineral transformations of natural clays with increasing temperature were studied to establish reference groups based on raw-material composition and high-temperature mineralogy. This study should be of interest to the local ceramic industry and should contribute to a more precise correlation between the composition of ancient ceramic and potential raw materials in further ancient ceramics studies, namely its provenance.

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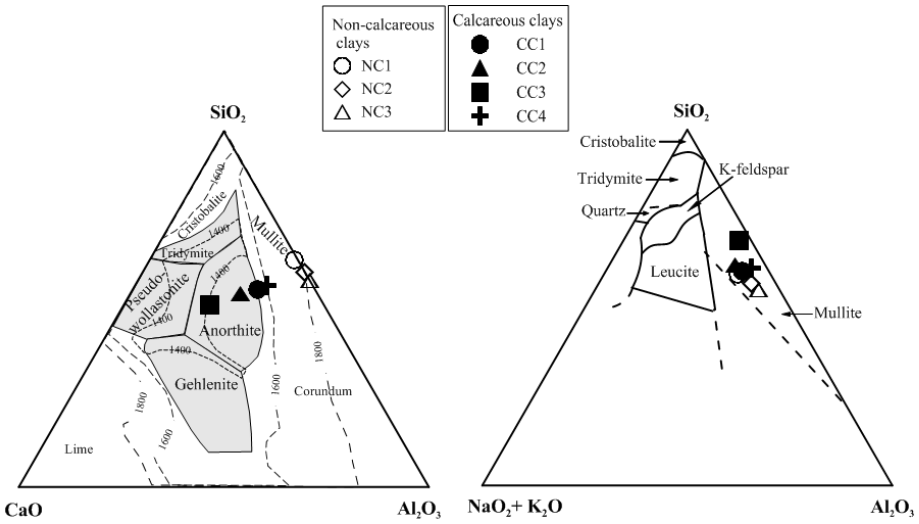
Figure captions

Figure 1. $SiO_2/Al_2O_3/CaO$ and $SiO_2/Al_2O_3/NaO_2+K_2O$ equilibrium diagrams (Levin *et al.*, 1964).



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372 **Figure 2**. Example of X-ray powder diffraction patterns of calcareous (CC1) and non-
373 calcareous clays (NC3) at different heating temperature.

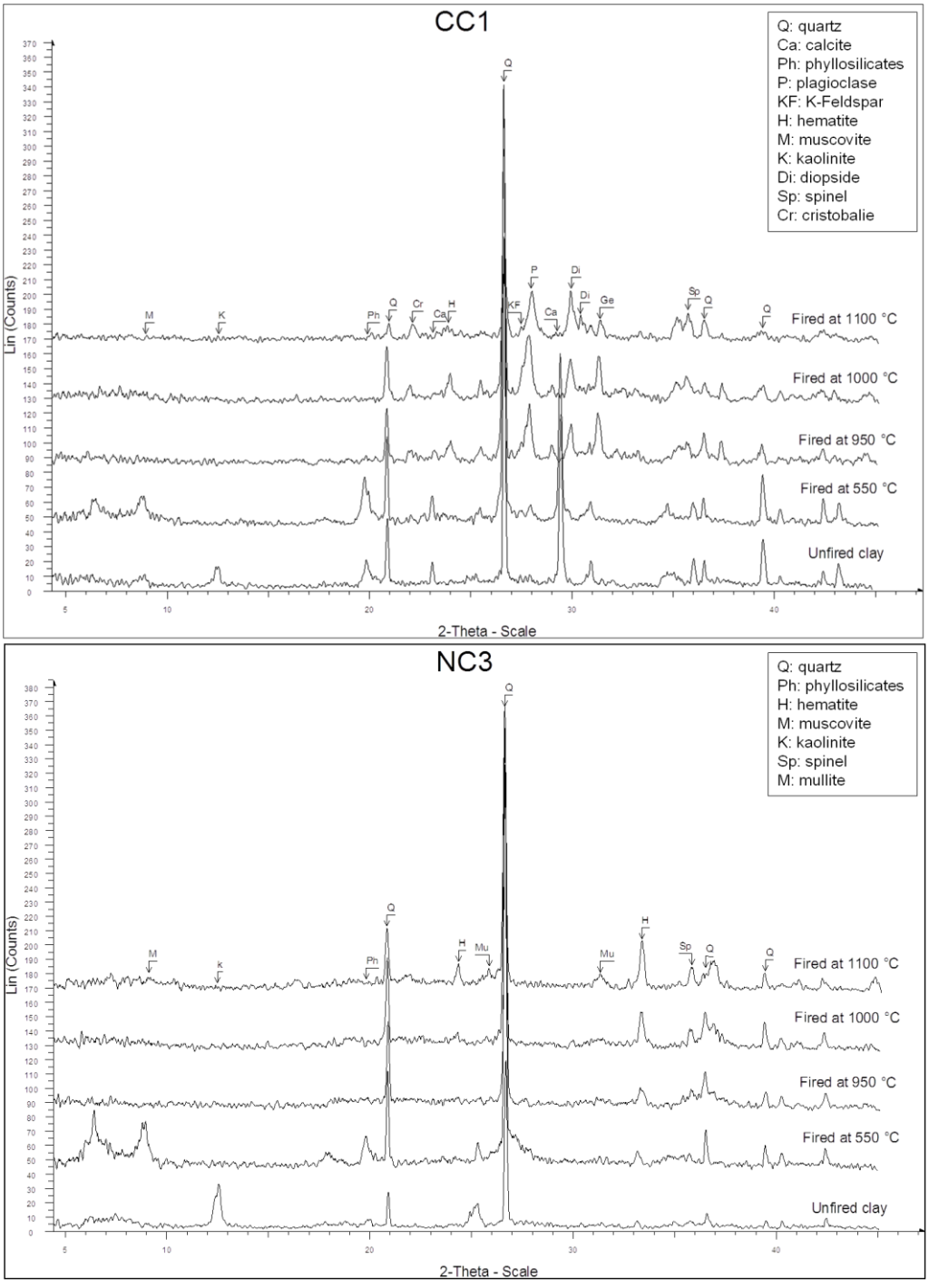

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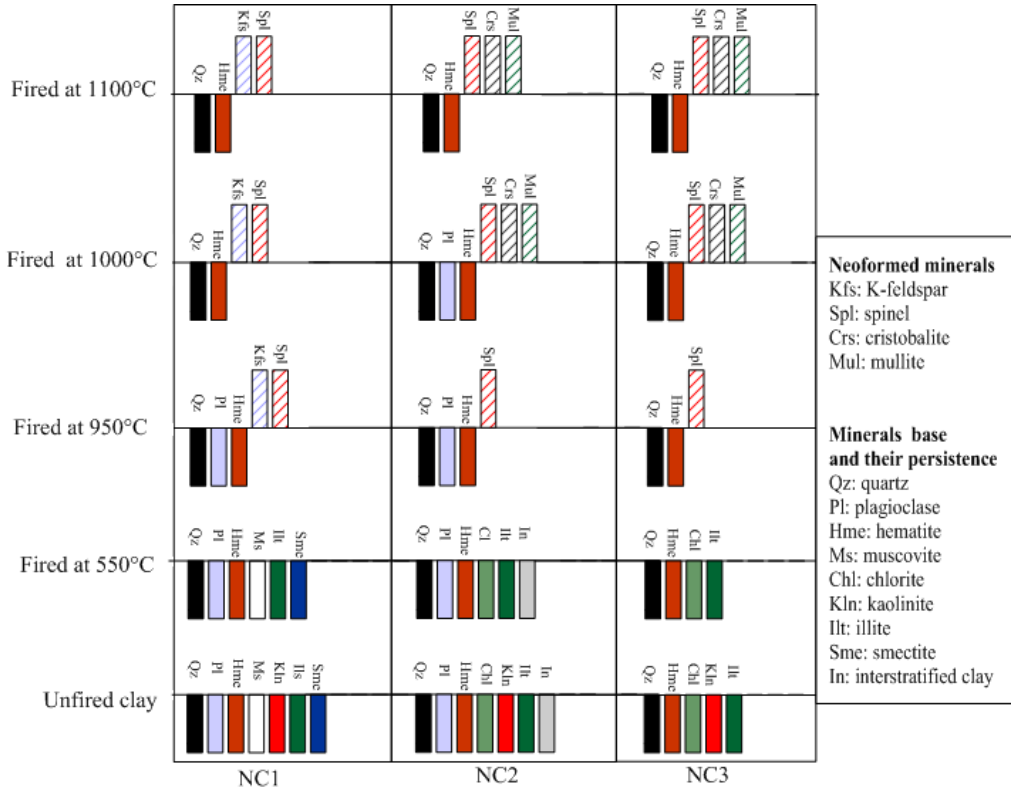
Figure 3. Mineralogical transformations of non-calcareous (a) or calcareous clays (b) during firing.



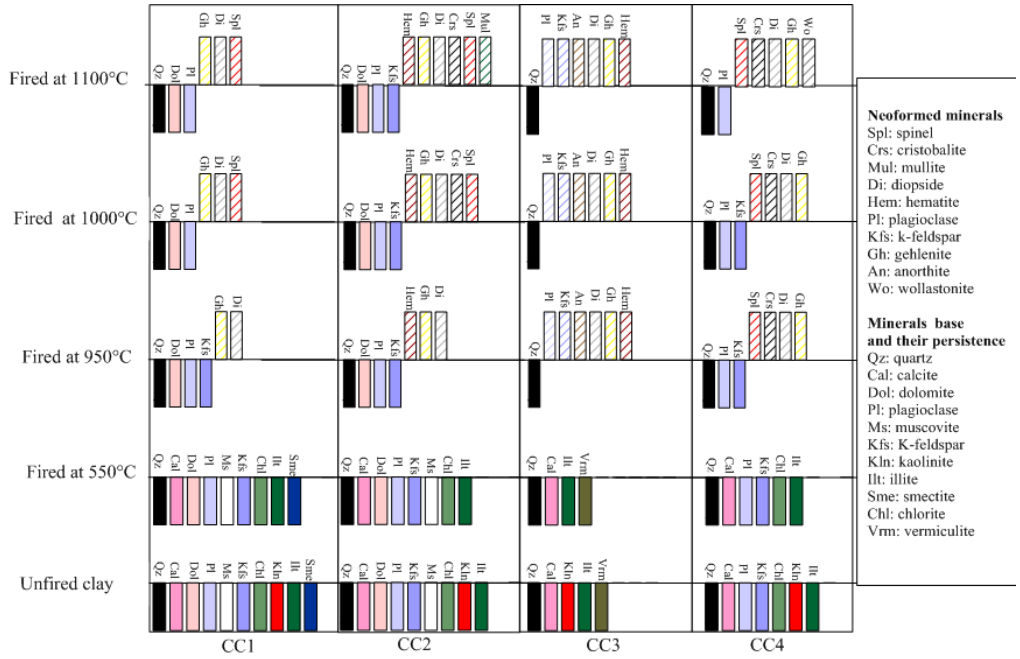
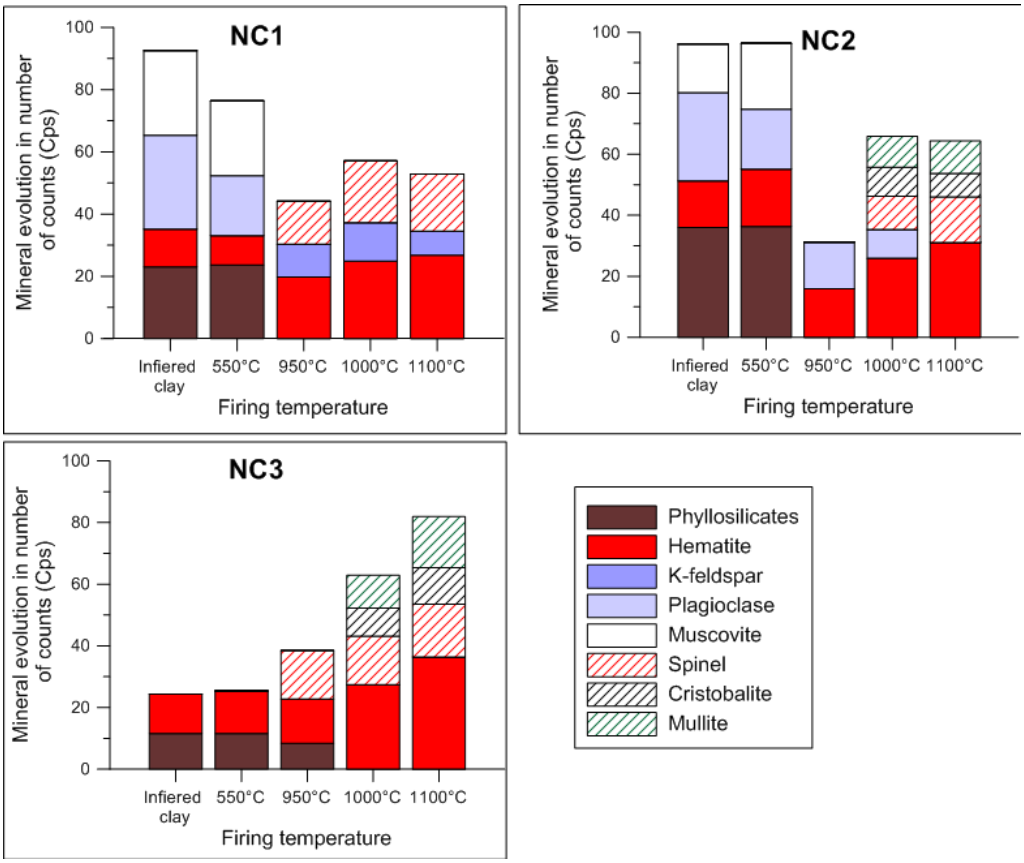


Figure 4. Evolution of raw and neoformed mineral contents from non-calcareous (a) or calcareous clays (b) with temperature.


NC1
NC2
NC3
Mineral evolution in number of counts (Cps)
Infiered clay
550°C
950°C
1000°C
1100°C
Firing temperature
Phyllosilicates
Hematite
K-feldspar
Plagioclase
Muscovite
Spinel
Cristobalite
Mullite

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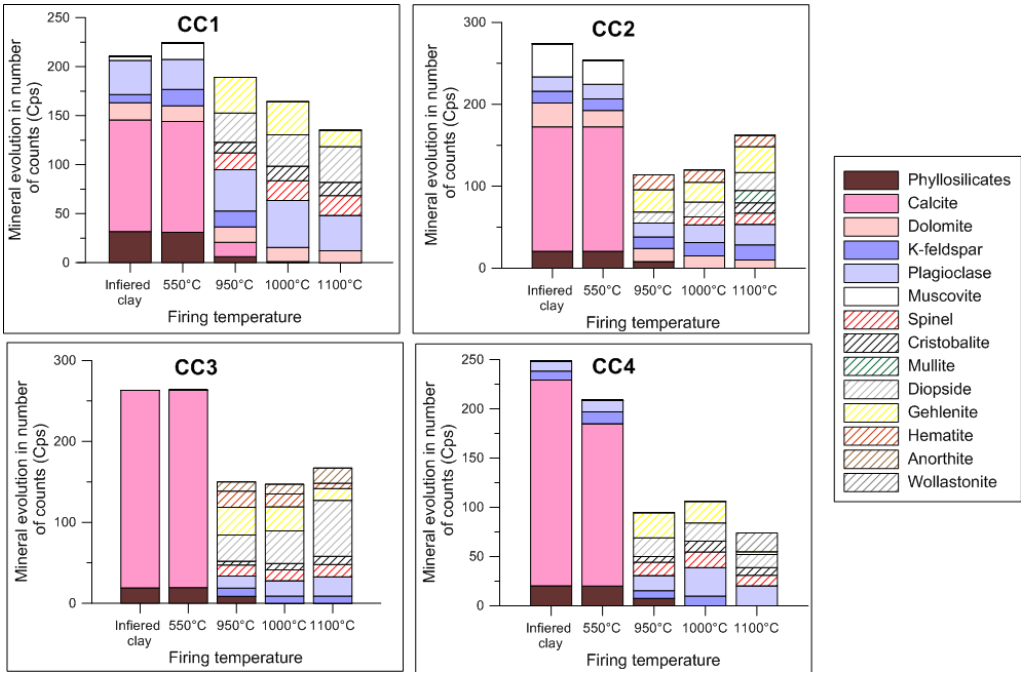
CC1
CC2
CC3
CC4
Mineral evolution in number of counts (Cps)
Infiered clay
550°C
950°C
1000°C
1100°C
Firing temperature
Phyllosilicates
Calcite
Dolomite
K-feldspar
Plagioclase
Muscovite
Spinel
Cristobalite
Mullite
Diopside
Gehlenite
Hematite
Anorthite
Wollastonite

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Figure 5. Quartz evolution in calcareous and non-calcareous clays according to temperature evolution, in number of counts (cps).

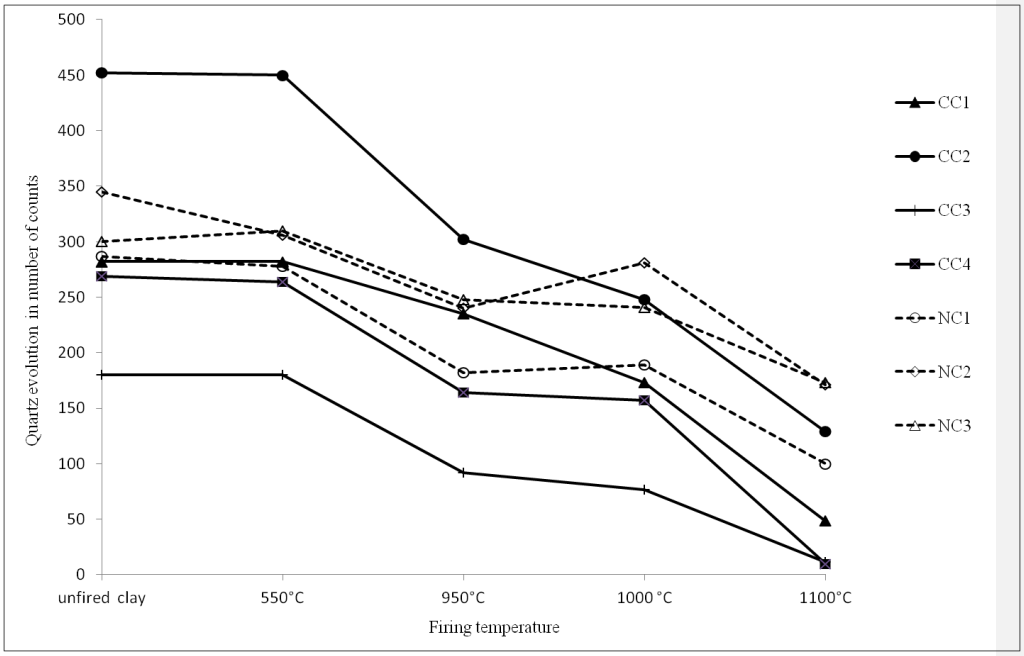

Table captions

Table 1. Chemical composition (wt.%) of the studied raw clay. Data from (El Ouahabi *et al.*, 2014a).

	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MnO (%)	MgO (%)	Na_2O (%)	K_2O (%)	TiO_2 (%)	P_2O_5 (%)	SO_2 (%)	Total (%)	L.O.I[a] (%)
NC1	48.2	26.6	15.6	0.6	0.1	2.2	1.3	5.0	0.7	0.2	0.0	100	9.1
NC2	51.5	33.8	0.5	0.0	1.8	1.9	4.4	1.0	0.2	0.1	6.6	100	6.6
NC3	47.6	34.5	0.4	0.0	2.4	1.1	3.3	1.0	0.1	0.0	9.0	99.4	9.0
CC1	44.9	24.8	5.1	11.4	0.1	2.7	0.8	4.1	0.8	0.3	0.2	95.2	17.8
CC2	41.2	20.4	8.3	14.4	0.1	2.8	0.8	4.2	0.7	0.4	0.0	93.3	16.6
CC3	35.4	14.6	12.5	19.2	0.1	0.9	0.2	1.3	0.5	0.5	0.0	85.2	22.6
CC4	45.9	26.2	11.1	9.0	0.0	1.4	0.7	2.2	0.8	0.6	0.0	97.9	15.8

[a] Loss on ignition at 1000 °C.

Table 2. List of mineral abbreviations used in this study, their chemical formula, and the diagnostic XRD peaks d(001) values) used for their identification (Whitney and Bernard, 2010).

Mineral	Abbreviation	Chemical formula	d value for (001) peak
Original minerals			
Quartz	Qz	SiO_2	3.34
Calcite	Cal	$CaCO_3$	3.04
Dolomite	Dol	$CaMg(CO_3)_2$	2.89
Kaolinite	Kln	$Al_2Si_2O_5(OH)_4$	7.18
Muscovite	Ms	$KAl_2[(OH)_2AlSi_3O_{10}]$	10.0
Clay minerals	Cl	[a]$(AlSi_2O_5^{2-})_n$	4.48
Original and neoformed minerals			
K-feldspar	Kfs	$(K,Na)AlSi_3O_8$	3.25
Hematite	Hem	Fe_2O_3	2.69
Plagioclase	Pl	$(Na,Ca)(Si,Al)_4O_8$	3.19
Neoformed minerals			
Cristobalite	Crs	SiO_2	4.05
Gehlenite	Gh	[a]$Ca_2Al_2SiO_7$	2.85
Mullite	Mul	$Al_6Si_2O_{13}$	3.40
Spinel	Spl	$MgAl_2O_4$	2.42
Wollastonite	Wo	$CaSiO_3$	3.31
Diopside	Di	$CaMgSi_2O_6$	2.99
Anorthite	An	CaAl2Si2O8	3.20

[a] simplified formula