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MODIFIED MINERAL PHASES DURING CLAY CERAMIC FIRING

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Abstract—Ceramic clays are among the most complicated of ceramic systems because of the very intricate relationship between the behavior of minerals during ceramic processing and their modifications during heating. A major challenge is to predict the phase changes in clay ceramics. The aims of this study were to establish reference data of ceramic products that can be formed based on the mineralogical compositions of the local raw materials. These data, in turn, can be compared with archeological ceramics in order to study their origins.

The mineralogical compositions and modifications during firing (550−1100ºC 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 distinguished according to the type of neoformed high-temperature minerals: non-calcareous clays and calcareous clays. For the non-calcareous raw materials, spinel was produced at 950ºC. Cristobalite and mullite were formed at temperatures in excess of 1000ºC from clays that contain illite, kaolinite, and chlorite. In clays containing vermiculite and large amounts of chlorite, hematite was formed at temperatures in excess of 950ºC. 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 carbonate content exceeds 10%.

Key Words—Ceramic, Clay, Phase modifications, Raw Materials, X-ray Powder Diffraction.

INTRODUCTION

Clay minerals undergo a complex set of thermal modifications during heating (Jordán *et al*., 2001; Pardo *et al*., 2011) which determine the final properties of the ceramic products. A major challenge is to predict the phase changes in fired ceramic clays because complex relationships exist between the structural and chemical properties of the fired ceramics.

Upon firing, the minerals in the fired ceramic clays undergo chemical and structural modifications from the original clayey materials. The high-temperature, low-pressure mineral modifications are influenced mainly by the chemical and mineralogical compositions of the raw materials, the maximum heating temperature, the heating rate, the duration of firing, and the kiln redox atmosphere (Brown and Bailey, 1963; Khalfaoui and Hajjaji, 2009).

Fired ceramic clays have a complex mineralogical composition, which makes the study of the destruction of mineral phases present in the raw material and the phases formed by firing rather complex (Jordán *et al*., 2001). Because the minerals of the raw materials partially decompose and form other phases upon crossing beyond their stability limits during firing, recognizing the influence of the pre-firing minerals on the products of firing is difficult (Jordán *et al*., 1999).

The present study focuses on the mineral modifications with increasing temperature for seven clays, of highly varied mineralogy from northern Morocco, to assess their suitability for the production of ceramics. The main aim was to study the mineral modifications of natural clays with increasing temperature and to establish reference groups for local ceramic industries based on raw-material composition and high-temperature mineralogy. The present study may be of use in archeological studies to establish provenance of ancient Moroccan ceramic clays.

MATERIALS AND METHODS

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

Seven samples were 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 experi-

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ments to study mineral changes during the ceramic firing process. The main compositional criteria were related to (1) the presence/absence of carbonates, and their composition (calcite or dolomite) and abundance, (2) the type(s) of phyllosilicates (clay minerals), their relative proportions, and (3) the presence/absence of Fe-rich minerals (hematite). Having established mineralogical compositions, two groups of clays were identified, one rich in carbonates (CC) and the other, non-calcareous (NC). The presence of types of carbonates (calcite or dolomite) affects the firing behavior and crystallization of minerals at high temperatures (Trindade *et al*., 2010).

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

Seven clay samples were oven dried at 35ºC for 48 h. Dried clay was ground and sieved through a 20 mm sieve to simulate industrial pressing conditions. Each clay sample was wetted in 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 a shaded and ventilated room. The dried samples (24 h in a shaded room plus 12 h at 105ºC in an oven) were kiln-fired at different temperatures (550, 950, 1000, and 1100ºC) for 1 h at a rate of 10ºC/min. Mineralogical analysis of the fired samples was carried out by X-ray diffraction (XRD), using a Bruker D8-Advance diffractometer with CuKα radiation (Department of Geology, University of Liege, Belgium) on powdered bulk sediment following the procedure described by Moore and Reynolds (1997). The powder XRD patterns were treated by the *DIFFRAC^{Plus} EVA* software (BRUKER, University of Liege, Belgium) to remove the background noise and to calculate profile parameters such as line positions and peak intensities. The estimation of mineralogical composition (Table 2) is based on the maximum count rate at the top of each characteristic d_{001} peak.

The abundances of selected elements (Si, Al, Fe, Ca, Mn, Mg, Na, K, Ti, P, and S) were measured as oxides on 2 g of dried and homogenized powder of clayey samples using X-ray fluorescence (XRF, Bruker S8 Tiger wavelength-dispersive X-ray fluorescence spectrometer) equipped with a Rh anticathode (Department of Ecology and Environmental Sciences, Umeå University, Sweden). Reproducibilities were >99% except for S (89%) and P (97%). More information about the method and the calibration can be found in a study by De Vleeschouwer *et al*. (2011). The same powdered samples were heated to 1000ºC for 2 h to determine the loss on ignition (L.O.I.).

RESULTS AND DISCUSSION

The clay ceramics industries usually use chemical data (XRF) to predict the formation of new crystalline phases during firing. The implications of carbonates and non-calcareous clays in the formation of the glassy phase, mullite, and cristobalite are interpreted by using $SiO_2/Al_2O_3/(NaO_2+K_2O)$ and $SiO_2/Al_2O_3/CaO$ equilibrium diagrams (Figure 1). The chemical compositions of the original phases plot within the mullite stability field on the $SiO_2/Al_2O_3/(NaO_2+K_2O)$ diagram (Figure 1). According to Khalfaoui and Hajjaji (2009), mullite is derived from the Al content, and this is related to the presence of clay minerals and mica-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 prevents the formation of the mullite. Decomposed clay minerals form, in combination with CaO, phases such as gehlenite, anorthite, and wollastonite, rather than mullite (Trindade *et al*., 2009, 2010). For the silica-rich material, cristobalite 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 (Figures 2, 3a,b) and related discussion of mineralogical modifications as a function of temperature are based on the two groups of raw materials defined

Table 1. Chemical composition (wt.%) of the raw clays studied (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 1000ºC.

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Table 2. Minerals, chemical formulae, and the diagnostic XRD peaks (d_{001}) used for identification in the present study.

Mineral	Abbreviation[a]	Chemical formula	d_{001} (Å)
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	[b] $(AlSi_2O_5^{2-})_n$	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	$Ca_2Al_2SiO_7$	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	$CaAl_2Si_2O_8$	3.20

[a] mineral abbreviations from (Whitney and Evans, 2010)
[b] simplified formula

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 modifications (Figures 2, 3a,b) observed with increasing temperature included the dehydroxylation of kaolinite at temperatures below 550ºC, followed by other clay minerals (illite, chlorite, smectite, and vermiculite), which dehydroxylated close to 950ºC. Calcite and dolomite altered into lime (CaO) and then reacted with other components to produce new

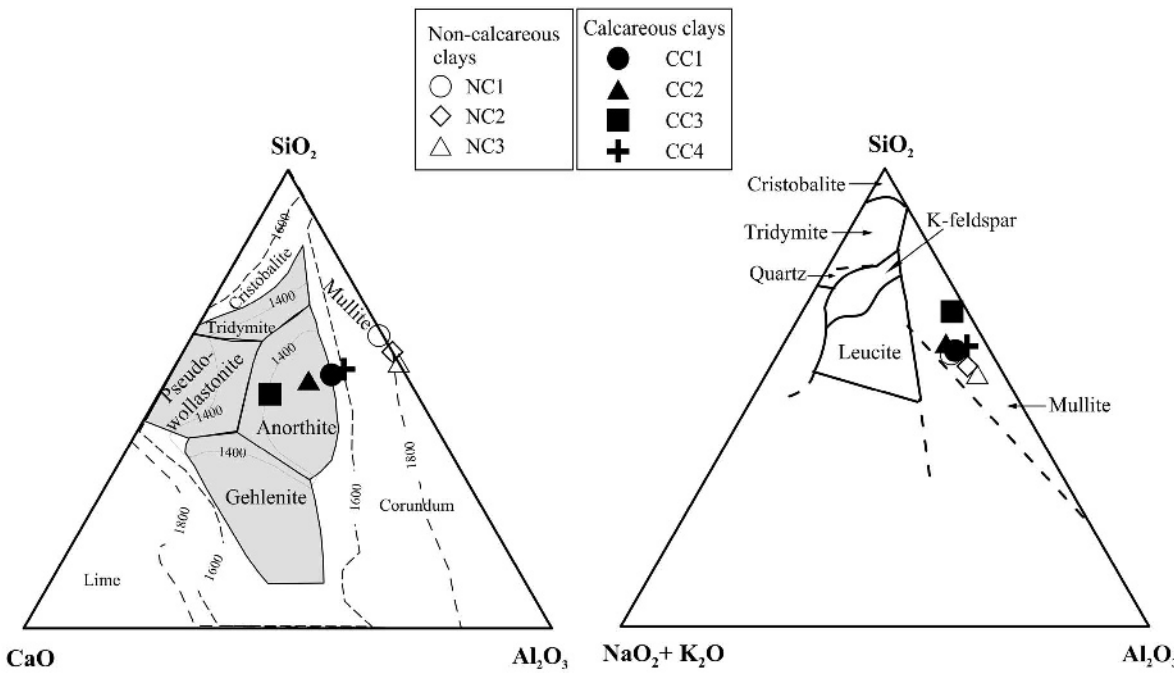


Figure 1. $SiO_2/Al_2O_3/CaO$ and $SiO_2/Al_2O_3/(NaO_2+K_2O)$ equilibrium diagrams (Levin *et al.*, 1964).

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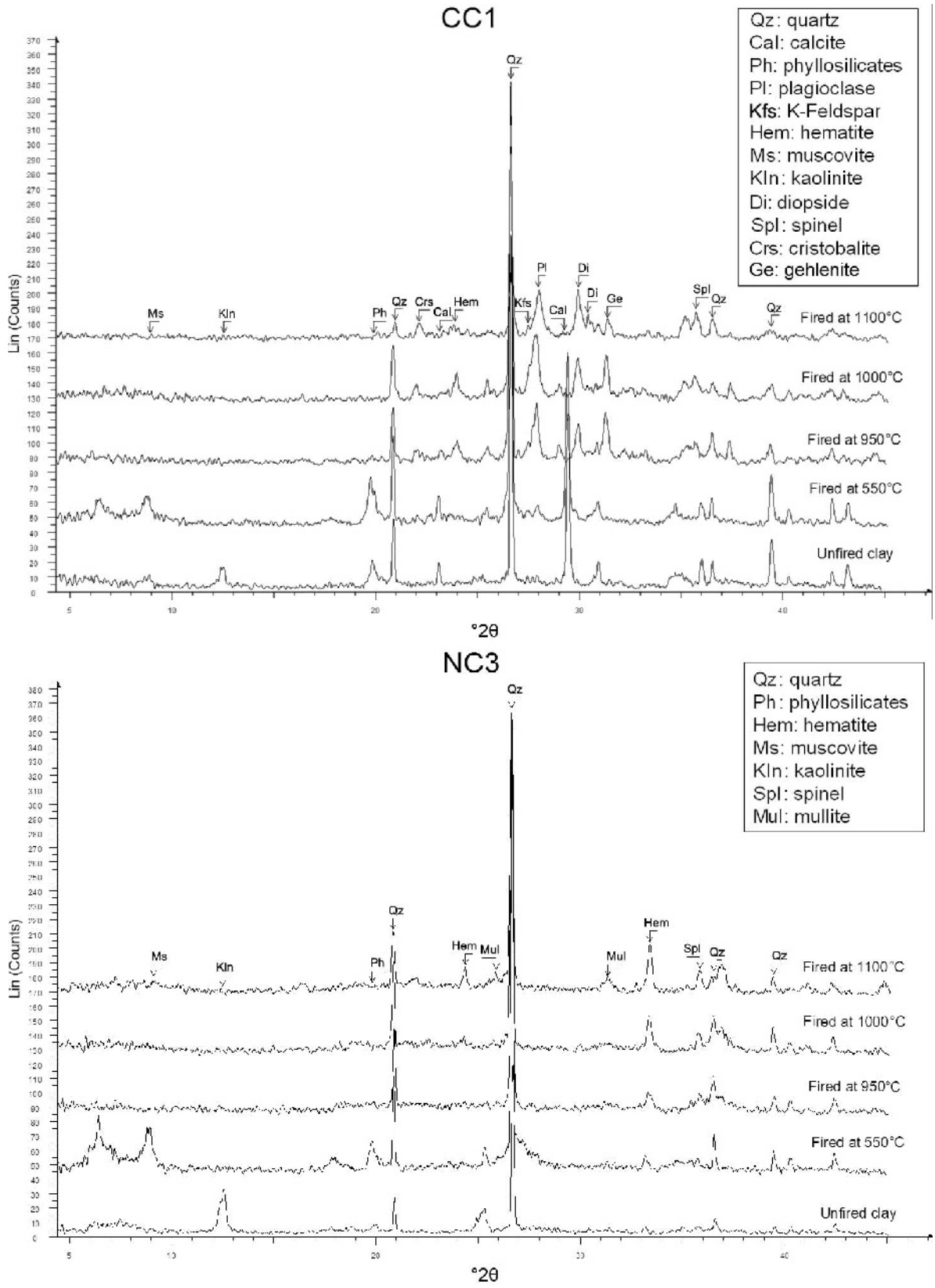


Figure 2. Example of powder XRD patterns of calcareous (CC1) and non-calcareous clays (NC3) at different heating temperatures.

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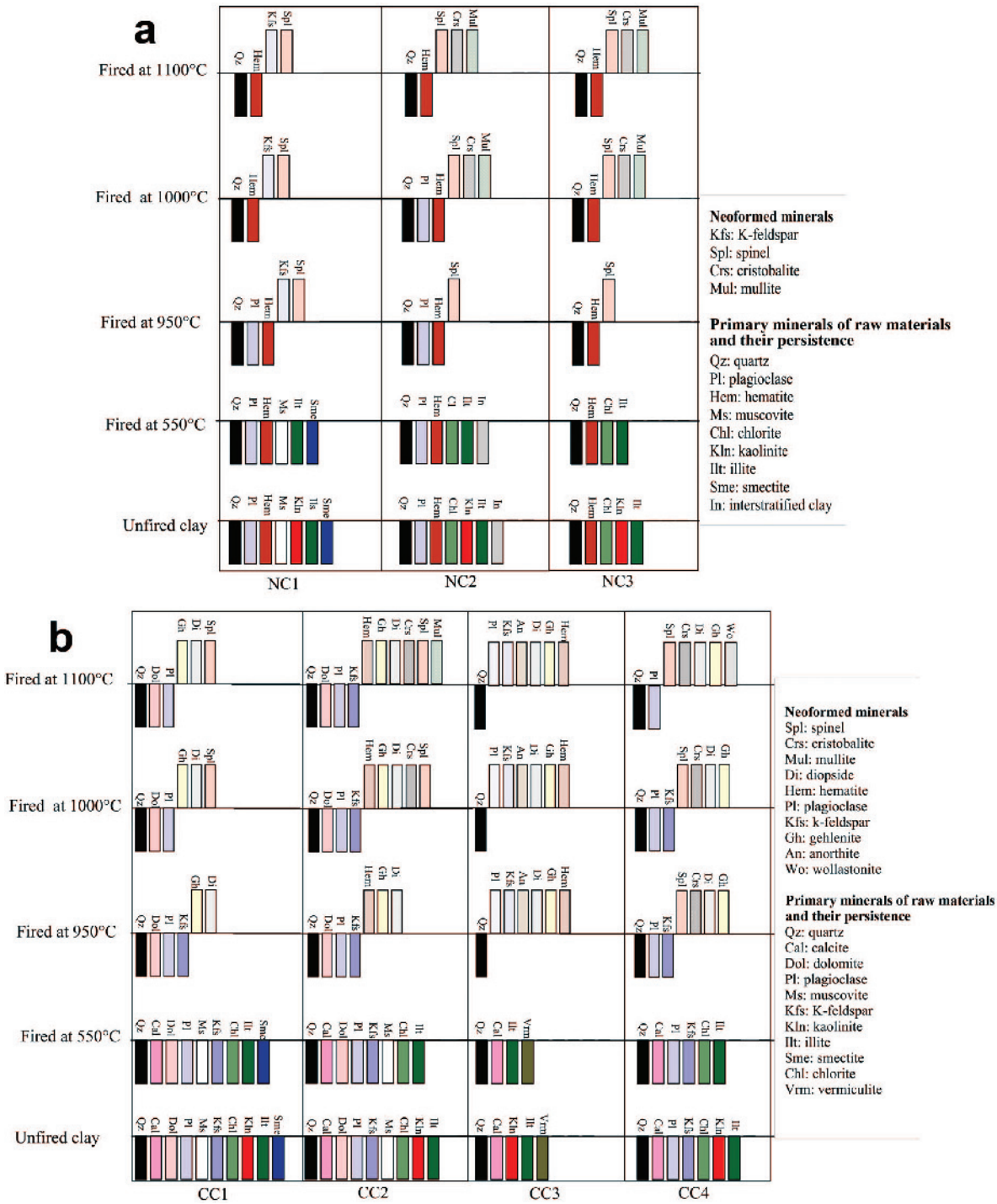


Figure 3. Mineralogical modifications of non-calcareous (a) or calcareous clays (b) during firing.

calcium minerals, such as gehlenite, diopside, and wollastonite (Trindade *et al*., 2009). Generally, K-feldspars disappeared at temperatures below 1000ºC, plagioclase seemed to persist up to 1100ºC, and quartz was preserved even at 1100ºC.

Non-calcareous clays

The three non-calcareous clay samples (NC1, NC2, and NC3) were kaolinitic and illitic clays with large quartz contents (Figures 3, 4a). Chlorite was only present in small amounts in samples NC2 and NC3. Smectite was present in NC1 (El Ouahabi *et al*., 2014b).

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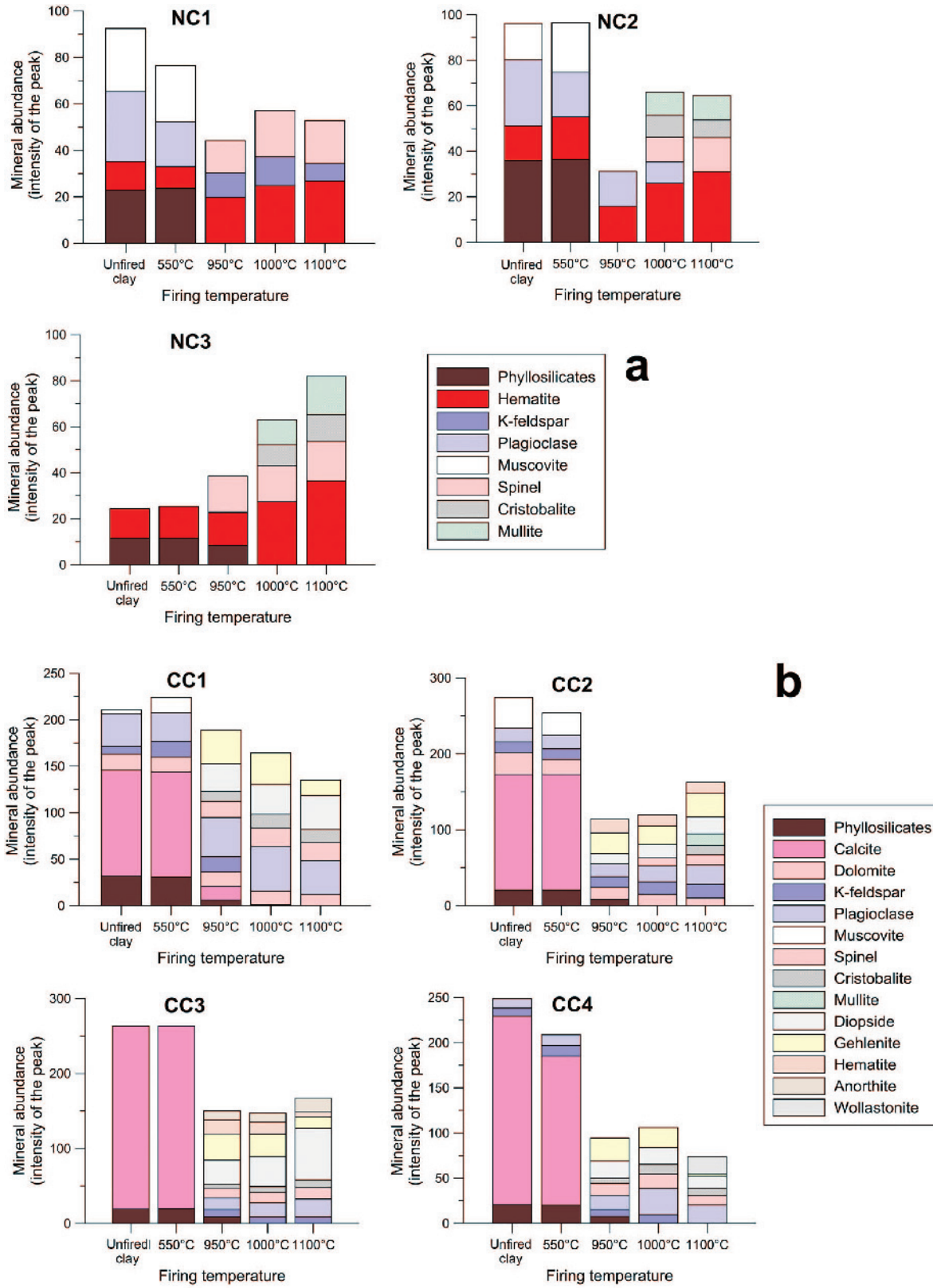


Figure 4. Variation of raw and produced mineral contents from non-calcareous (a) or calcareous (b) clays with temperature.

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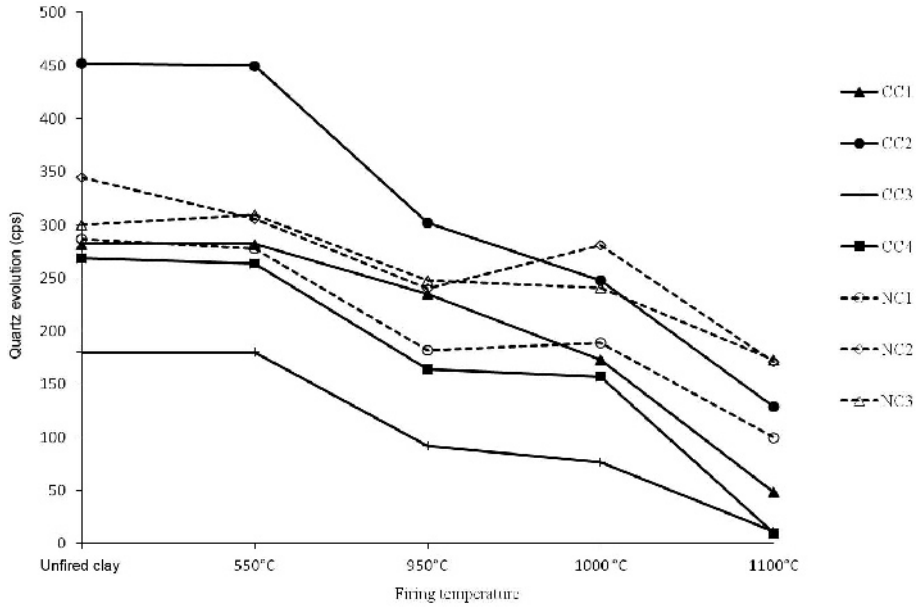


Figure 5. Quartz variation in calcareous and non-calcareous clays according to temperature variation, in number of counts (cps).

Small amounts of hematite were observed. Plagioclase was absent from NC3 clay.

A variety of mineral modifications occurred in NC1 (Figures 3a, 4a, 5). Kaolinite and illite-smectite disappeared at 550ºC and 950ºC, respectively. Plagioclase and muscovite disappeared close to 950ºC and were replaced by alkali feldspars. Quartz and hematite were present throughout the entire temperature range. Hematite increased slightly in abundance whereas quartz abundance was reduced by a factor of two at the maximum firing temperature. Newly formed mullite and K-feldspar appeared at 950ºC and reached their maximum abundances at 1100ºC.

Despite their different starting compositions, samples NC2 and NC3 showed similar formation of new minerals. Mineral modifications with firing included the loss of all phyllosilicates including muscovite from 950 to 1000ºC, and plagioclase at close to 1100ºC. Quartz and hematite persisted up to 1100ºC, with their maximum abundance at the maximum fired temperature. Spinel formed at 950ºC, followed by mullite and cristobalite at 1000ºC. Mullite and cristobalite were more abundant at 1100ºC.

All the fired samples studied contained Mg-rich spinel, probably derived from the dehydroxylation of chlorite and smectite, phyllosilicate minerals rich in MgO. Spinel was formed by the reaction: $MgO + Al_2O_3 \rightarrow MgAl_2O_4$. Cristobalite and mullite were found in samples NC2 and CN3, due to modification of phyllosilicates, particularly illite (Trindade *et al*., 2010). These two clays contained ~20% of muscovite and illite, respectively (El Ouahabi *et al*., 2014b). Cristobalite was probably produced by modification of quartz, as observed previously (Pardo *et al*., 2011). The major original mineral persisting at high temperature was quartz, which was the most abundant phase in all fired clay samples. The other pre-firing mineral accompanying quartz up to 1100ºC was hematite.

The assemblage of newly formed minerals from non-calcareous clays was relatively simple, consisting of spinel, cristobalite, mullite, and K-feldspar. Mullite appeared at 1000ºC in quartz-rich clays, and its abundance increased at higher temperatures (Figure 5). It appears that the quartz content (~50%) in combination with phyllosilicates promote the formation of mullite. Cristobalite was identified only in the quartz-rich clays (samples NC2 and NC3) at 1000ºC. The K-feldspar observed after firing at high temperatures in the NC1 clay is probably a high-temperature phase which replaced the illite-muscovite phase.

Firing below 950ºC produced no significant mineralogical modifications. Formation of firing products began from 950ºC. Feldspars (K-feldspar and plagioclase) that formed at 950ºC act as a flux that facilitated easy melting upon further firing. During clay firing, micaceous minerals, in particular, changed to mullite, K-feldspar, and plagioclase (Khalfaoui and Hajjaji, 2009).

Carbonate-rich clays

The four carbonate-rich clays (CC1-CC4) were kaolinitic and illitic clays (Figures 3b, 4b, 5), with large quartz contents. Chlorite was the major clay mineral phase in the CC1 sample, but occured at trace abundances in the other samples. In sample CC3, vermiculite was the principal clay mineral phase. Variable amounts of calcite were identified, and small amounts of dolomite, plagioclase, and K-feldspar were present in these carbonate clays (El Ouahabi *et al*., 2014b).

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For CC1, calcite and 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 newly formed minerals were gehlenite and diopside, which appeared at 950ºC, followed by spinel at 1000ºC. The gehlenite content decreased at higher temperatures, and diopside and spinel were more abundant at 1100ºC. K-feldspar disappeared at temperatures close to 950ºC; plagioclase seemed to persist up to 1100ºC, and increased in amount.

The mineralogical modifications reported in Figures 2 and 3b indicate that when the temperature was increased to 950ºC, $CaCO_3$ decomposed to CaO, phyllosilicates decomposed, and spinel-type phases appeared. CaO reacted with Si forming Ca-silicates such as gehlenite, diopside, and wollastonite. As the temperature increased further, the gehlenite content decreased.

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

Among the mineral modifications of CC3, kaolinite disappeared at 550ºC, whereas calcite and vermiculite persisted up to 950ºC. Quartz was the only phase present throughout the entire temperature range, with its abundance being very small at the maximum firing temperature. The newly formed phases were diverse: they included plagioclase, K-feldspar, diopside, gehlenite, and hematite. All newly formed phases appeared at 950ºC and were most abundant at 1100ºC, with the exception of hematite and gehlenite.

During firing of CC4, phyllosilicates disappeared at 950ºC and K-feldspar at 1000ºC. Very small amounts of plagioclase and quartz remained at the highest temperature of firing. Gehlenite, diopside, cristobalite, and spinel formed at 950ºC, and attained maximum abundance at 1000ºC. Later, relatively large amounts of wollastonite were formed at 1100ºC. The amounts of diopside, cristobalite, gehlenite, and spinel increased gradually.

The most significant mineralogical changes were observed in samples with carbonates when fired at T >800ºC. Firing caused the decomposition of carbonates, clay minerals, and silicates and the formation of a melt phase rich in Si, Al, Ca, and K (Trindade *et al*., 2009). From this melt phase, several phases crystallized, reacting continuously with increasing temperature.

All the fired calcareous clay samples contained gehlenite and diopside which formed due to the presence of $CaCO_3$. In addition, hematite, spinel, cristobalite, and anorthite were formed. Wollastonite formed only in CC4 at high temperature, close to 1100ºC. Melting started just before 950ºC when carbonates were present (Hajjaji and Kacim, 2004). Ca and Mg from carbonates may act as melting agents but they are reported to somehow limit the extent of vitrification at temperatures >1000ºC (Cultrone *et al*., 2001). On the other hand, the greater SiO_2 content in these samples provided a larger amount of potential silica-rich melt.

Gehlenite starts to form at temperatures between 550 and 950ºC, when Mg is absent, by reaction between CaO from carbonates, and Al_2O_3 and SiO_2 from the dehydroxylated phyllosilicates (Peters and Iberg, 1978). Diopside also started to form between 550 and 950ºC in all calcareous clays by reaction of Ca, Mg, and SiO_2 from dolomite and quartz for CC1 and CC2; Ca was probably supplied by calcite, however, and Mg seems to have come from vermiculite or chlorite for samples CC3 and CC4. Wollastonite probably formed from the reaction of CaO with SiO_2 at high temperature; its formation was marked mainly by a sharp decrease in quartz content (Figure 5). Wollastonite improves the strength as well as the water and heat resistances of ceramics (Azarov *et al*., 1995).

Newly formed hematite resulted from dehydroxylation of an Fe-rich clay, *i.e*. vermiculite in the present case. The amount of hematite increased in unfired clays upon heating which suggests that ferric oxide may be formed during the decomposition of clay minerals containing non-negligible amounts of iron (Nodari *et al*., 2007). At higher temperatures (1100ºC), phyllosilicates had already disappeared in all samples, having been modified into spinel for most clays, and further into mullite for CC2. Thus, the spinel phase essentially originated from decomposed chlorite, i.e. the principal Mg-bearing mineral. Spinel was absent from the firing products of clays that did not contain chlorite (CC3). Between temperatures of 550 and 950ºC, the appearance of the diffraction peaks at 3.2 Å, 3.18 Å, and 4.4 Å for CC3 indicated the formation of the calcium aluminum silicate phase, anorthite ($CaAl_2Si_2O_8$).

The most significant difference among the calcareous fired clays was the appearance of mullite and hematite in sample CC2 only at temperatures between 550 and 1000ºC. Mullite appeared at high temperature, which could be related to the presence of sufficient illite-muscovite. Illite and muscovite were fully consumed by 1100ºC; they reacted with quartz, and were modified into mullite plus a melt (Rodriguez-Navarro *et al*., 2003). During firing, Fe is evolved from the clay minerals that are generally responsible for the formation of mullite (Castellanos *et al*., 2012). The amount of plagioclase decreased slowly and K-feldspar decreased at 1000ºC. Feldspars (especially alkali feldspars) are fluxes, so they

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may be newly formed during firing, as demonstrated by their increase from 1000ºC, which can be attributed to the formation of mullite (Lee *et al*., 2008). Illite-muscovite underwent a change to mullite and K-feldspar, plus a melt (Rodriguez-Navarro *et al*., 2003).

In clays with small amounts of carbonates (<10%), samples CC1 and CC4, the fired clays consisted mainly of quartz, diopside, cristobalite, spinel, gehlenite, and wollastonite. Cristobalite appeared in the firing products of clays with large amounts of quartz. The absence of the mullite phase in those samples is noted; small quantities of carbonates (<10%) clearly inhibited the formation of mullite and instead formed Ca-rich aluminosilicates. Mullite was formed in carbonate-rich clays when the carbonates exceeded 10%, with sufficient Al (associated with the abundance of plagioclase and illite-muscovite). With a small amount of Al, anorthite was formed instead of mullite.

The results support the study of ceramic provenance by supporting the development of a compositional databank and establishing reference groups of ancient clay from Moroccan sites. Such study could help to answer some archeologists' questions concerning places and regions of origin, to determine techniques for the production of artefacts, and to interpret cultural influences. With the determination of the chemical and mineralogical composition of ceramic sherds, therefore, it will be possible to relate it to a specific clay source and conditions of production, namely the firing temperature. This study might be useful in supporting provenance studies of ancient Moroccan ceramic clays.

CONCLUSIONS

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 was controlled by the initial mineralogical composition, in particular the carbonate mineral content.

Firing non-calcareous raw materials produced spinel at temperatures of between 550 and 950ºC. Cristobalite and mullite were formed at temperatures >1000ºC from clays that contained illite, kaolinite, and chlorite. In clays containing vermiculite and a large amount of chlorite, hematite was formed at temperatures between 550 and 950ºC.

In firing products of calcareous clays, Ca-silicates (diopside, gehlenite, and wollastonite) were accompanied by spinel, cristobalite, mullite, hematite, and feldspars. The presence of small amounts of carbonates inhibited mullite formation, and instead Ca-silicates (gehlenite and wollastonite) were formed. When the carbonates exceeded 10%, mullite was formed, but its formation depended on the quantity of Al. When there was insufficient Al to form mullite then a small amount of anorthite was formed instead.

The modifications of minerals in 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 ceramics industry and should contribute to a more precise correlation between the composition of ancient ceramics and potential raw materials in further ancient-ceramics studies.

REFERENCES

Azarov, G.M., Maiorova, E.V., Oborina, M.A., and Belyakov, A.V. (1995) Wollastonite raw materials and their applications (a review). *Glass and Ceramics*, **52**, 237–240.

Brown, G.E. and Bailey, S.W. (1963) Chlorite polytypism: II. Crystal structure of a one-layer Cr-chlorite. *American Mineralogist*, **48**, 42–61.

Castellanos, A., Mauricio, O., Ríos, R., Alberto, C., Ramos, G., Angel, M., Plaza, P., and Vinicio, E. (2012) A comparative study of mineralogical transformations in fired clays from the Laboyos Valley, Upper Magdalena Basin (Colombia). *Boletin de Geología*, **34**, 43–55.

Cultrone, G., Rodriguez-Navarro, C., Sebastian, E., Cazalla, O., and Torre, M.J.D.L. (2001) Carbonate and silicate phase reactions during ceramic firing. *European Journal of Mineralogy*, **13**, 621–634.

De Vleeschouwer, F., Renson, V., Claeys, P., Nys, K., and Bindler, R. (2011) Quantitative WD-XRF calibration for small ceramic samples and their source material. *Geoarchaeology*, **26**, 440–450.

El Ouahabi, M., Daoudi, L., De Vleeschouwer, F., Bindler, R., and Fagel, N. (2014a) Potentiality of clay raw materials from northern Morocco in ceramic industry: Tetouan and Meknes areas. *Journal of Minerals and Materials Characterization and Engineering*, **2**, 145–159.

El Ouahabi, M., Daoudi, L., and Fagel, N. (2014b) Preliminary mineralogical and geotechnical characterization of clays from Morocco: Application to ceramic industry. *Clay Minerals*, **49**, 1–17.

Hajjaji, M. and Kacim, S. (2004) Clay-calcite mixes: Sintering and phase formation. *British Ceramic Transactions*, **103**, 29–32.

Jordán, M.M., Boix, A., Sanfeliu, T., and de la Fuente, C. (1999) Firing transformations of Cretaceous clays used in the manufacturing of ceramic tiles. *Applied Clay Science*, **14**, 225–234.

Jordán, M.M., Sanfeliu, T., and de la Fuente, C. (2001) Firing transformations of Tertiary clays used in the manufacturing of ceramic tile bodies. *Applied Clay Science*, **20**, 87–95.

Khalfaoui, A. and Hajjaji, M. (2009) A chloritic-illitic clay from Morocco: Temperature-time-transformation and neoformation. *Applied Clay Science*, **45**, 83–89.

Lee, W.E., Souza, G.P., McConville, C.J., Tarvornpanich, T., and Iqbal, Y. (2008) Mullite formation in clays and clay-derived vitreous ceramics. *Journal of the European Ceramic Society*, **28**, 465–471.

Levin, E.M., Robbins, C.R., and McMurdie, H.F. (1964) *Phase Diagrams for Ceramists.* American Ceramic Society, Columbus, Ohio, USA.

Moore, D.M. and Reynolds, R.C. (1997) *X-ray Diffraction and the Identification and Analysis of Clay Minerals*. Oxford University Press, Oxford, UK.

Nodari, L., Marcuz, E., Maritan, L., Mazzoli, C., and Russo, U. (2007) Hematite nucleation and growth in the firing of carbonate-rich clay for pottery production. *Journal of the European Ceramic Society*, **27**, 4665–4673.

Pardo, F., Meseguer, S., Jordán, M.M., Sanfeliu, T., and

https://doi.org/10.1346/CCMN.2015.0630506 Published online by Cambridge University Press

González, I. (2011) Firing transformations of Chilean clays for the manufacture of ceramic tile bodies. *Applied Clay Science*, **51**, 147–150.

Peters, T. and Iberg, R. (1978) Mineralogical changes during firing of calcium-rich brick clays. *Ceramic Bulletin*, **57**, 503–509.

Rodriguez-Navarro, C., Cultrone, G., Sanchez-Navas, A., and Sebastian, E. (2003) TEM study of mullite growth after muscovite breakdown. *American Mineralogist*, **88**, 713–724.

Trindade, M.J., Dias, M.I., Coroado, J., and Rocha, F. (2009) Mineralogical transformations of calcareous-rich clays with firing: A comparative study between calcite and dolomite-rich clays from Algarve, Portugal. *Applied Clay Science*, **42**, 345–355.

Trindade, M.J., Dias, M.I., Coroado, J., and Rocha, F. (2010) Firing tests on clay-rich raw materials from the Algarve Basin (southern Portugal): Study of mineral transformations with temperature. *Clays and Clay Minerals*, **58**, 188–204.

Whitney, D.L. and Evans, B.W. (2010) Abbreviations for names of rock-forming minerals. *American Mineralogist*, **95**, 185–187.

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https://doi.org/10.1346/CCMN.2015.0630506 Published online by Cambridge University Press