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Firing process of natural clays. Some microtextures and related phase compositions

P. Duminuco[a,*], B. Messiga[a], M.P. Riccardi[b]

[a] *Dipartimento di Scienze della Terra, Università di Pavia, via Ferrata, 1, 27100 Pavia, Italy*
[b] *C.G.S. – Centro Grandi Strumenti, Università di Pavia, via A. Bassi, 21, 27100 Pavia, Italy*

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Abstract

Microtextural and microchemical data on sherds, experimentally fired at different temperatures, reveal the presence of non-homogeneous compositions of firing phases, even over a distance of 10–30 μm. These results were obtained with an analytical strategy combining bulk and 'in situ' (spot) analyses. Such microtextures, formed by sub-solidus reactions, occur in limited domains of the system, testify for a short-range diffusion of chemical components during the firing process, even if 1050°C were reached in the kiln. Relationships among phases formed during the firing process indicate that their composition is independent of kiln temperatures and is related to the composition of precursor phases on which they grow. The use of data obtained by X-ray diffraction techniques on bulk samples, when used to define firing temperatures of historical artifacts, could be considered.

Thermal analysis shows the different steps of the process in terms of fluid-releasing reactions and indicates some constraints to the development of the reaction. © 1998 Elsevier Science B.V.

Keywords: Firing; Microprobe analysis; Mineral reactions; Natural clay; Thermogravimetric analysis

1. Introduction

Firing temperatures are commonly used in archeometric researches to determine the technological attributes of an historical sherd and to deduce some of the aspects of the material of a given historical period [1–3]. Current methods used in archeometry are mainly based on the presence of particular minerals detected by 'bulk' investigations (X-ray diffractometry). The appearance of a particular firing mineral phase assemblage is related to the temperature reached in the kiln. In particular, the reaction involving gehlenite ($Ca_2Al_2SiO_7$, geh), quartz (SiO_2, qz), wollastonite ($CaSiO_3$, wo) and anorthite ($CaAl_2Si_2O_8$, an), namely

$$\mathrm{geh} + 2\mathrm{qz} \rightarrow \mathrm{wo} + \mathrm{an} \qquad (1)$$

is considered to be diagnostic for the attainment of particular temperatures being reached during the firing. It is found that wollastonite and anorthite are stable in the sherd for temperatures exceeding 950°C [4].

The aim of this paper is to contribute to a better calibration of firing temperatures, recorded by both historical and present-day artifacts. Consequently, clay artifacts are considered as artificial rocks formed in a kiln. The methodological approach is the same

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*Corresponding author. Tel.: +39 382 505879; fax: +39 382 5058890; e-mail: pia@elicona.unipv.it

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as that used when petrological investigations on metamorphic rocks are carried out [5,6]. The microtextural relationships existing among mineral assemblages developed during firing are used to emphasise the role played by reaction kinetics on the control of the growth characteristics and firing phase compositions.

For these purposes, experiments were undertaken on clay samples in order to assess some of the kinetic factors constraining the occurrence of new phases developed on particular microdomains, as a result of reactions occurring between a clay matrix and temper grains during the firing process. Each sample is considered to be representative of the attainment of steady-state equilibrium conditions. The progress of reactions has been investigated through microtextural and microchemical analyses of samples fired at different temperatures.

Our results stress the presence of non-stoichiometric firing phases formed in a clay matrix. The role exerted by fluid-evolving reactions (de-hydration and de-carbonation), during temperature rise, in the development of new phases were also studied by thermogravimetric analysis (DTG).

2. Experimental

Experiments were carried out on two samples of contrasting bulk composition (Ca-rich and Ca-poor clay), Fig. 1. Fragments (50–150 µm) of natural minerals such as feldspar (albite, $NaAlSi_3O_8$), mica (biotite, $K(Fe,Mg)_3AlSi_3O_{10}(OH)_2$) and calcite (cc, $CaCO_3$) were added to the raw clay material in an amount not exceeding 10% by volume. Experimental runs were carried out at temperatures of 550°, 850° and 1050°C. After 14 h at peak temperature, samples were cooled in 10 h.

The study combines analytical data produced with 'bulk' and 'in-situ' techniques [7]. The 'bulk' analyses were produced using powder X-ray diffraction (XRD) and X-ray fluorescence (XRF). The electron microprobe (EMP) was employed to perform the 'in-situ' (spot) analyses on polished, C-coated thin sections. Microtextural investigations under optical (OM) and electron (EM) microscopes were carried out.

The analytical data were collected by means of the following instruments:

A

Wt %	*Ca-rich*	*Ca-poor*
SiO_2	51.96	60.41
TiO_2	0.57	0.88
Al_2O_3	16.23	19.93
Fe_2O_3	4.89	6.51
MnO	0.10	0.12
MgO	3.29	2.58
CaO	8.83	1.41
Na_2O	0.70	0.86
K_2O	2.57	1.69
P_2O_5	0.10	0.09
LOI	10.75	5.52

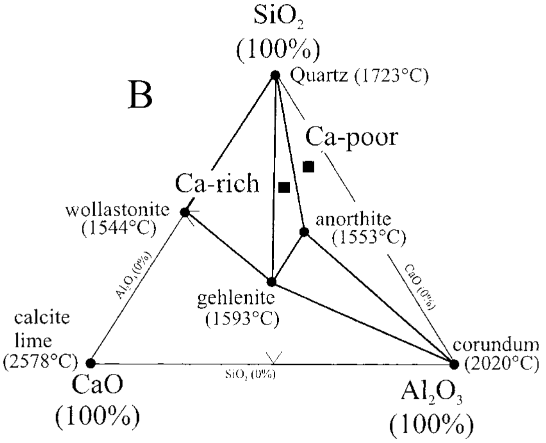

Fig. 1. Compositions of Ca-rich and Ca-poor clay (■) reported on ACS (Al_2O_3-CaO-SiO_2) diagram (B) and in the table (A). Mineral compositions and compatible phases are also shown by full dots and tie lines, respectively.

XRD: X-ray analyses were carried out on Philips PW 1800, CuK_α graphite-monochromatised radiation, diffractometer on random 'powder' preparations. The X-ray diffraction data were analysed considering the intensity of reflections diagnostic for each mineral.

XRF: major element analysed of Philips PW 1480; Rh and W tubes were employed according to the analysed element in the 1600–3000 W range.

XRF data have been obtained on powder pellets (2 g).

EMP and EM, a JEOL JXA 840A electron microanalyser equipped with three wavelength dispersive spectrometers (TAP, PET and LIF analysing crystals) and one Si(Li) energy dispersive spectrometer (Be window) was used. Analytical conditions of 20 KW of accelerating voltage and 20 ηA were employed with a spot size of 5 μm. Data were collected by the WDS (wavelength-dispersive spectrometer) and processed with the TASK correction programme. Mineral phases were used as standards, to avoid matrix effects. The estimated precision was ca. 3% for major and 10% for minors elements. Samples are prepared as polished thin section, C-coated.

DTA 1600 cell of du Pont (USA) assembled with a 910 DSC module; experiments were carried out in static air, scan speed 10 K min^{-1}. DTA is controlled by a TA 2000 system. The instrument was previously calibrated with an NaCl standard.

3. Results and discussion

Firing phases in Ca-rich clays lay across the ACS (Al_2O_3–CaO–SiO_2) triangle between clay minerals and calcite ($CaCO_3$) compositions, whereas Ca-poor clays are restricted on the AS side of the triangle (Fig. 2(B)). The bulk composition of the system controls the extent of phase compositional variability, as evidenced by Ca-rich clays [7].

In Ca-rich clay, a simplified mass balance may be used to model the firing reaction. Illite ($KAl_4Si_7O_{20}(OH)_4$) (ill) and calcite (cc) represent the phases present in the natural clay, whereas K-feldspar ($KAlSi_3O_8$) (kfd) and gehlenite ($Ca_2Al_2SiO_7$) (geh) are the firing phases. Silica is considered as an excess phase in this calculation.

$$0.4\,\mathrm{ill} + 1.2\,\mathrm{cc} \rightarrow 0.4\,\mathrm{kfd} + 0.6\,\mathrm{geh} + 1.0SiO_2 + 1.6H_2O + 1.2CO_2 \quad (2)$$

Based on mineral chemistry, the identification of phases growing on clay matrix is rather difficult, since they do not retain stoichiometric compositions. In the Ca-rich sample, fired at 1050°C, the 'in-situ' analysed compositions are superposed on the melilites field and, even when non-stoichiometric, may be considered as a complex solid solution of different melilite end-members (Fig. 3). In fact, XRD reveals the presence of melilites in the bulk [7].

Fig. 3 displays compositional distinct layers bounding the pristine tempered minerals. As a rule, the phase positions indicate a compositional array between

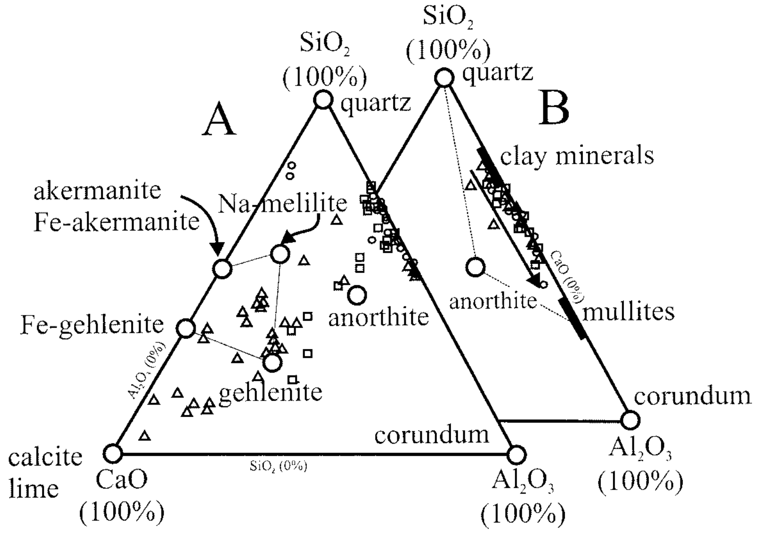

Fig. 2. ACS diagrams show the chemical compositions of firing phases in (A) Ca-rich clay and (B) Ca-poor clay at (open dots) 550°C, (squares) 850°C, and (triangles) 1050°C. The pure phases are represented by white dots. The shaded area encloses the melilites compositional field.

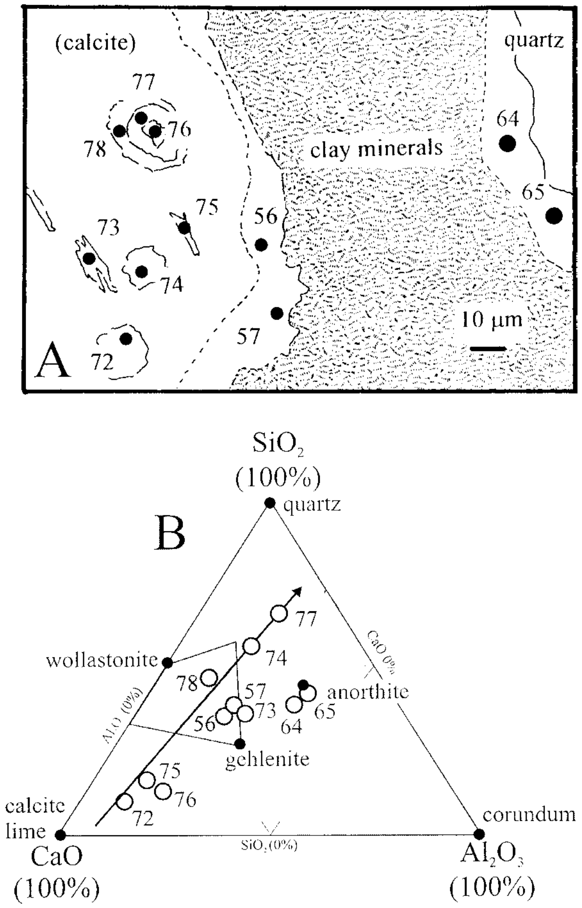

Fig. 3. Experimental firing carried out at 1050°C. (A) Key microtexture in which reactions occurring between temper fragments and clay matrix are shown. Black dots represent spots analyses. (B) Phase compositions obtained by EMP analyses (open dots). The pure phases are represented by full dots. The shaded area encloses the melilites compositional field.

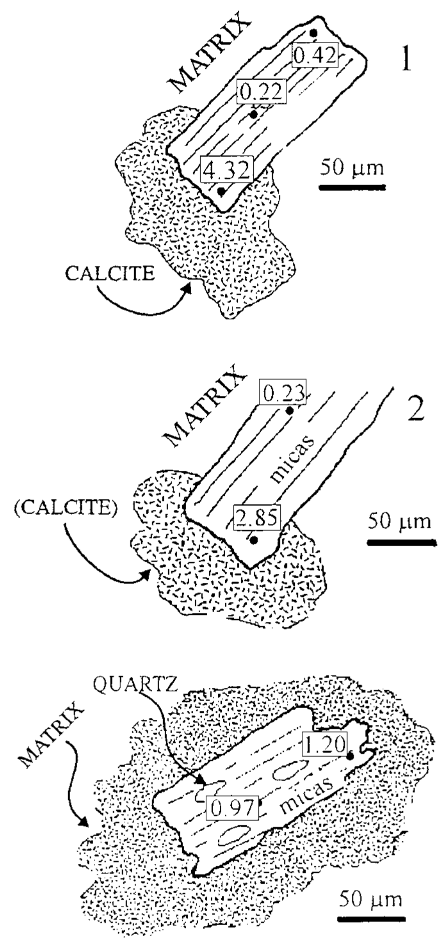

Fig. 4. Conceptual scheme showing the Ca-contents in biotites fixed at (1) 550°C, (2) 850°C and (3) 1050°C. Black dots are spot analysis positions. Numbers in labels represent the CaO contents (wt %).

calcite and clay minerals. The presence of chemically complex phases is related to the particular microtexture. Some analyses of samples, fired at 1050°C, match the gehlenite compositions, in particular the rim of calcite grain (e.g. 56 and 57). Within the calcite sites some grains have a complex zoning (e.g. 76, 77, 78) even at a distance of few tens of µm. Other grains display a more homogeneous composition (e.g. 72, 73, 74, 75). Anorthite-bearing compositions are restricted to the rims bounding quartz grains (e.g. 64, 65). These layers are produced by reactions of temper minerals with the adjacent clay-matrix. The different chemistries of layered minerals and their compositional zoning reveals the chemical control exerted by the reacting phases. Such transient mineral assemblages are produced by sub-solidus reactions occurring in limited domains of the system and testify for a short-range diffusion of chemical components during the firing process, even if 1050°C were reached in the kiln.

In the Ca-rich clay, the biotite changes its original composition during the increase in firing temperature. In a reaction behaviour controlled by the presence of calcite, Fig. 4 evidences a Ca compositional zoning occurring at lower temperatures (550°C). At 850°C,

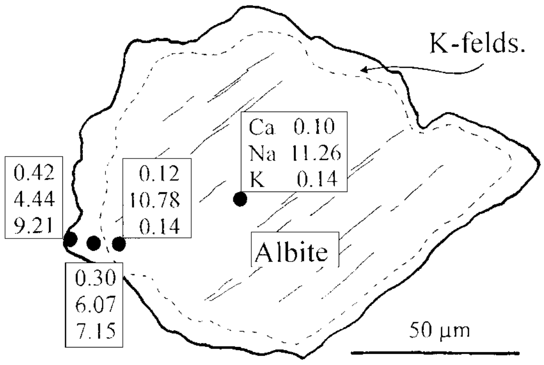

Fig. 5. Compositional zoning of albite fragment reached during the 1050°C firing. Labels contain values for CaO, Na_2O and K_2O (wt%). Dots represent spot-analysis positions.

the Ca compositional gradient is strongly reduced. Finally, at 1050°C, biotite reaches a more homogeneous composition but retains appreciable amounts of Ca. The increase in temperature produces compositionally homogeneous phases by enlarging the reaction domains and enhancing chemical communication among phases. This latter aspect could be related to chemical changes produced in biotite by the highest firing temperatures, leading to an amorphous and anhydrous phase [8].

At temperatures exceeding 850°C, albite changes its composition by reaction with the clay matrix. A rim of K-feldspar ($KAlSi_3O_8$) overgrows the albite crystals in the sample fired at 1050°C, according to the mass balance reaction (reaction 2). The zoning pattern is characterised by a steep decrease in the Na content with a concomitant increase of K (Fig. 5). In this case, the K-feldspar rim is crystalline, as testified by its optical characters detected under OP microscope, and displays stoichiometric compositions, as evidenced by EMP analyses.

The breakdown of calcite occurs ca. 850°C and releases CO_2 as a component of the fluid phase in Ca-rich clays (Fig. 6). In the sample the amount of fluid loss was ca. 12 wt%. The formation of a secondary porosity during the rise in temperature may be due to the release of fluid phase. The formation of pores, partially filled by crystal aggregates of firing phases with a well-developed crystalline habit, has already been described [9]. This seems to indicate that the system is not completely open to fluids. In fact, the fluid phase released by reactions produces a transient fluid pore pressure leading to the mineral crystallisation within pores.

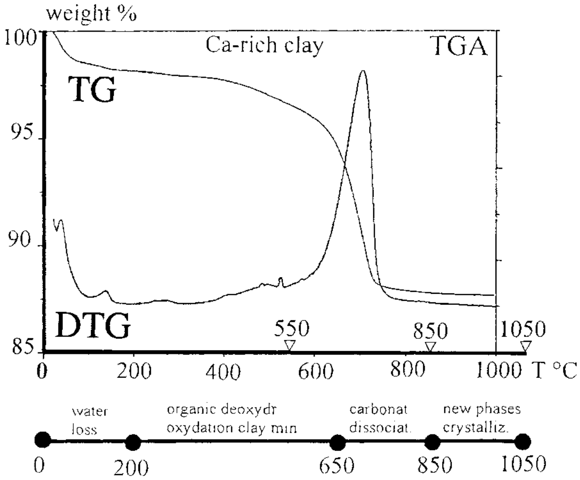

Fig. 6. TGA of Ca-rich clay. Triangles represent temperature of experimental run.

4. Conclusions

The results obtained lead to the following conclusions:

Ca-poor clay did not show the wide compositional variability of firing phases as displayed by Ca-rich ones. In this aspect, the calcium derived from calcite breakdown may produce a compositional array of phases such as gehlenite, anorthite, wollastonite (diopside).

The presence of a fluid phase may be considered responsible for the enhancement of reaction kinetics and for the increase of ‘chemical communications’ among reacting phases. This lead to an enlargement of the reaction domains within the sherd.

Relationships among phases formed during the firing process indicate that their composition is independent of kiln temperatures and is related to the composition of precursor phases on which they grow. On this aspect, the use of bulk analysis to define firing temperatures could be critically considered. In a system partially reacted and equilibrated, the obtained temperatures could be misleading. The relationships existing between temperature increase and reduction of the biotite zoning as well as the growth of K-feldspar rim on albite could be significant. Both could be microchemical features, suitable to evaluate the attainment of certain *T*-values in the kiln.

In the clay matrix, the crystallisation of phases with a non-stoichiometric composition could be due to differences between the rate of nucleation and growth of phases and the rate of temperature increase. In particular, if the firing rate is faster than nucleation and growth rate, we may conclude that the presence of composition is well established and homogeneous phases could be inhibited. This occurs because new phases nucleate in a reaction behaviour characterised by the breakdown reaction of the crystal lattices of clay minerals. Exceptions are the K-feldspars occurring as rims around albite. In this case, the similarity between albite and K-feldspar crystal lattices drives the epitactic reactions governing the compositional zoning.

Acknowledgements

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References

[1] R.B. Heimann, Archeomater. 3 (1989) 123.
[2] F. Veniale, in: Analytical Methodologies for the Investigation of Damaged Stones, Advanced Workshop, Pavia, Italy, 1990, p. 1.
[3] M. Maggetti, Forthschr. Mineral. 64 (1986) 87.
[4] T.J. Peters, R. Iberg, Am. Ceram. Soc. Bull. 57 (1978) 503.
[5] J.B. Thompson, in: P.H. Albeson (Ed.), Researches in Geochemistry, New York, John Wiley, 1959, pp. 427.
[6] R. Joensten, Geochim. Cosmochim. Acta 41 (1977) 649.
[7] P. Duminuco, M.P. Riccardi, B. Messiga, M. Setti, Ceramurgia 5 (1996) 281.
[8] P. Duminuco, B. Messiga, M.P. Riccardi, in: Le Scienze della Terra e l'Archeometria, Seconda Giornata Nazionale, Rovereto, Italy, 1995, pp. 137.
[9] M. Dondi, G. Ercolani, G. Guarini, M. Marsigli, I. Venturi, Ceramurgia 6 (1995) 301.