Applied Clay Science 15 (1999) 337–366

Clay materials for ceramic tiles from the Sassuolo District (Northern Apennines, Italy). Geology, composition and technological properties

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Received 18 November 1998; accepted 4 May 1999

Abstract

In the Sassuolo area (northern Italy) there is the largest tilemaking district in the world, which has practically served over the past years as an industrial scale laboratory for assessing the technological properties of clays and their suitability for the production of wall and floor tiles. The local clays are recovered from different geological units and distinguished in two principal types, with clearly differentiated compositions and technological properties: ‘‘marly clays’’ and ‘‘red shales’’. These local clays, which 20 years ago constituted the sole mineral resource of the Sassuolo District, now supply only 40% of the demand. This trend is largely connected with both process innovation (wet grinding, fast firing, etc.) and product changes (from red to white bodies). Overall, approximately 2 million tpa of clay materials are used in coloured bodies: marly clays for wall tiles (majolica, ‘‘birapida’’, ‘‘monoporosa’’) and red shales for both floor tiles (glazed red stoneware) and wall tiles (‘‘monoporosa’’). © 1999 Elsevier Science B.V. All rights reserved.

Keywords: ceramic clays; technological properties; clay mineralogy; grain size distribution; chemical composition; ceramic traditional uses; Northern Italy

1. Introduction

The Sassuolo Ceramic District (Modena and Reggio Emilia Provinces, northern Italy) has the highest concentration in the world of tilemaking plants

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PII: S0169-1317(99)00027-7

(approximately 300), with an annual output of around 450 million square metres, accounting for approximately one-sixth of the global production.

This industrial district developed during the sixties and seventies, partly thanks to the wide availability of clay raw materials having suitable technological properties (Palmonari et al., 1974) for both wall tiles (majolica) and floor tiles (red stoneware and ‘‘cottoforte’’). In the eighties, the area saw a significant technological innovation, leading to a complete restructuring of the production process, with the introduction of wet grinding with spray drying, as well as fast drying and firing cycles in mono-layer roller kilns (Fiori and Fabbri, 1985; Bertolani et al., 1986). In this way, the Italian tile industry became the world leader in technology and plant, creating new types of products by fast single firing which met with remarkable commercial success (single-fired stoneware, porcelain stoneware, ‘‘monoporosa’’).

However, the fast production cycles imposed drastic modifications to the ceramic bodies, with a marked reduction in the clay component in favour of complementary materials (feldspars, quartz-feldspathic rocks, etc.). At the same time, there was also a significant variation in the technological requirements for clay raw materials, with preference being given — especially in the nineties — to light-coloured bodies obtained from imported raw materials, at the expense of local clays which yield products with a reddish colour and different performance characteristics (Fabbri and Fiori, 1985; Fiori et al., 1989; Fabbri and Dondi, 1994). These trends also led to a gradual reduction in the contribution of Apennine clays to the overall consumption of the Sassuolo District: in fact, consumption dropped from 95% local clays in 1980 to about 40% in 1998.

Notwithstanding these trends, the demand for local clays dropped only moderately, from about 2.5 million tons in the early eighties to about 2 million tons in 1997, principally due to the strong increase in tile production during the same period. This strong demand for local clays was met by exploiting diverse geological sources, capable of supplying raw materials with different technological characteristics. This sector, too, has seen many changes: from about 130 clay quarries active in the Sassuolo area during the past forty years, only about twenty are currently still in operation.

Within this context of continuous change, this paper proposes to delineate a general and up-to-date picture of the use of local clays in the Sassuolo District, through a critical revision of the existing literature. The objectives are the following:

- to review the characteristics of the clay deposits according to the most recent data on the geology of the northern Apennines;
- to uniform the chemical and mineralogical data for the various clay sources;
- to synthesise and normalise the technological data, taking into account the requirements imposed by the current production cycles for ceramic tiles;
- to identify industry trends in the use of local clays, attempting to correlate the changes observed over time with the characteristics of the raw materials.

2. Methodological approach

The bibliography for the clays of the Sassuolo District is fairly abundant and includes references both to the geological and compositional characteristics of the deposits, as well as to the technological aspects connected with ceramic production. However, interpretation of these data is made difficult because they are non-homogeneous and not directly comparable, having been obtained by different methods and often using non-standardised test procedures.

For example, the geological descriptions of the deposits are often generic or obsolete, and do not always permit a definite identification of the type of clay. To overcome this obstacle, a census was taken of the quarries which were active in the period between 1960 and 1998, systematically verifying the stratigraphic attributions on the basis of the new cartography (Geological Map of Emilian Apennines, 1986–1997) and the most recent geological knowledge (Bettelli et al., 1987a,b; Gasperi et al., 1987; Martelli et al., 1998).

As regards the composition of the clays, the literature includes some 90 chemical analyses of the major elements (obtained in large part by XRF spectrometry), accompanied by qualitative mineralogical analyses conducted by X-ray powder diffraction. The quantitative mineralogical composition was calculated, for all samples, by a computerised method, on the basis of the chemical and X-ray diffraction data. The grain size distribution data were obtained by sedimentation (Andreasen pipette) or X-ray monitoring with Micromeritics SediGraph 5100 apparatus.

The articles consulted contain references to different technological properties of the clays: plasticity (Atterberg limits), methylene blue index (MBI), behaviour under pressing (pressing expansion and green bending strength), drying (drying shrinkage and dry bending strength) and firing (firing shrinkage, water absorption and fired bending strength). The water absorption was determined according to the EN 99 standard or by equivalent methods, while the EN 100 standard was generally used for bending strength. The dimensional variations were thus defined: pressing expansion $[100(L_p - L_m)L_m^{-1}]$, drying shrinkage $[100(L_p - L_d)L_p^{-1}]$ and firing shrinkage $[100(L_m - L_f)L_m^{-1}]$, where L_m is the length of the mould and L_p, L_d and L_f are the length of the pressed, dried and fired specimen respectively.

For the firing behaviour, two maximum temperatures were considered: approximately 1000°C with traditional cycle (24–36 h cold-to-cold) and approximately 1150°C with fast cycle (60 min cold-to-cold).

3. Geology of the clay deposits

The northern Apennines have an extremely complex geological structure, characterised by a series of overthrusted tectonic nappes with N–NE vergence

(Ligurian units and Tuscan nappe). To the south of Sassuolo, in particular, the Ligurian Units, ranging in age from Lower Cretaceous to Lower Eocene, were deposited at different times between Middle Eocene and Upper Miocene (Bettelli et al., 1987b). During this period, syntectonic sedimentation caused the formation of the thick Epiligurian sequences in piggy-back basins (Bettelli et al., 1987a). Moreover, at the margin between the Apennines and the Po Valley plain there is a more recent band of sediments (Pliocene–Quaternary), defined as semi-autochthonous because they were subjected to moderate tectonic movements (Gasperi et al., 1987).

The clays used by the ceramic industry come from different formations belonging to both the Ligurian and Epiligurian Units, as well as to the successions of the apenninic margin (Fig. 1 and Table 1).

3.1. Semi autochthonous sediments

Along the apenninic margin there are outcrops of prevalently pelitic sequences, within which three different lithostratigraphic units have been identified (Gasperi et al., 1987): Rio del Petrolio Fm (Lower Pliocene), Marano Fm (Middle Pliocene), Torrente Tiepido Fm (Upper Pliocene?–Lower Pleistocene). The Pliocene Formations were deposited in unconformity on the Ligurian or Epiligurian units, while the Torrente Tiepido Fm lies in paraconformity on the Rio del Petrolio Fm. (Fig. 2A).

The mineral exploitation of these Formations was facilitated by their closeness to the Sassuolo tilemaking plants, and by certain other favourable conditions: uniform lithology (grey–blue marly clays), thicknesses of a few hundred metres with a gradual dip of strata (10°–30°) and absence of major tectonic disturbances.

There are outcrops of Torrente Tiepido Fm principally in the band between the Secchia and Panaro Rivers, mined particularly along the Corlo River (Fig. 3A). Outcrops of Rio del Petrolio Fm are located mostly west of the River Secchia, and its mining has essentially taken place in the Rocca River valley. The clays of the Marano Fm are situated east of the Panaro River and have been poorly exploited, fundamentally due to their greater distance from Sassuolo.

3.2. Epiligurian units

This is a succession of five Formations (Montepiano, Ranzano, Antognola, Bismantova, Termina) deposited in ample synclines, as much as thousands of metres thick, in discordance on the Ligurian Units (Bettelli et al., 1987a). However, the ceramic industry has exclusively exploited the basal portion of the succession, and in particular the Montepiano and Ranzano Formations (Middle Eocene–Lower Oligocene), whose outcrops are principally in the western part of the Sassuolo District (Fig. 2B).

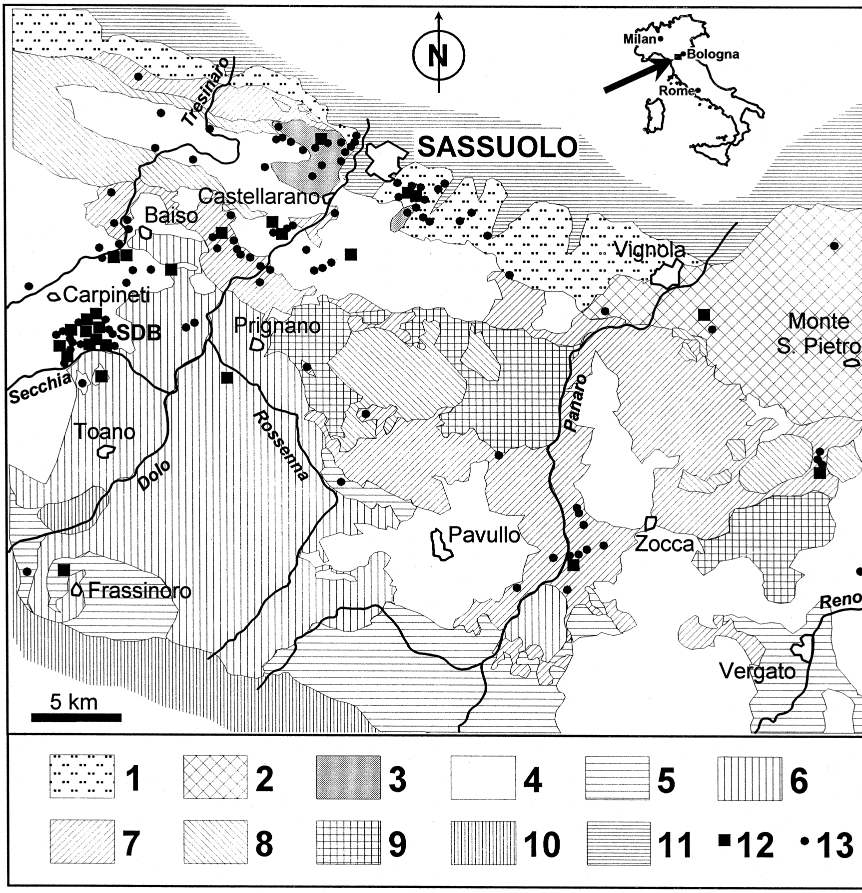


Fig. 1. Simplified geological map of the northern Apennines around the Sassuolo Ceramic District (modified after Bettelli et al., 1987b). Apenninic margin (Pliocene–Pleistocene): Torrente Tiepido Fm (1), Marano Fm (2) and Rio del Petrolio Fm (3). Eocene–Miocene Epi-Ligurian sequences (4). Ligurian units (Cretaceous–Eocene): Basal Complex Ligurid I (5), Monghidoro Unit and Val Rossenna melange (6), Basal Complex Ligurid II (7), Cassio Unit (8), Coscogno tectonic melange (9). Tuscan Nappe (10). Quaternary continental deposits (11). Quarries: active (12) and abandoned (13). SDB: Secchia–Dorgola Basin.

The Ranzano Fm is characterised by notable lithological variability on a regional scale, with half a dozen members distinguished on the basis of different ratios between pelites, sandstones and conglomerates (Martelli et al., 1998). The ceramic industry utilises only the pelitic lithotypes, which constitute almost the entire upper part of the Unit between the Secchia and Tresinaro valleys (Varano de' Melegari Member). These are apparently very uniform successions passing in paraconformity to the overlying Antognola Fm, which in the past has often been confused with the Ranzano shales. Overall, the Ranzano Fm is the most important resource for ceramic production in Sassuolo, with a dozen quarries currently active. These are situated in the Secchia–Dorgola Basin (Fig. 3B) and

Table 1
Geological features of clay materials for ceramic tiles from the Sassuolo District

Geological unit	Age	Lithology	Thickness	Sedimentary environment	Structural unit
Torrente Tiepido Fm	lower Pleistocene	dark gray to blue–gray marly clays with sandy intercalations	200–600 m		
Marano Fm	middle–upper Pliocene	gray to blue–gray marly clays with sandy intercalations	150–300 m	neritic and coastal deposits in thin to very thick strata	Apenninic margin (Semi autochthonous sequences)
Rio del Petrolio Fm	lower Pliocene	whitish, gray and blue–gray marly clays	100–400 m		
Ranzano Fm (Varano de' Melegari member)	lower Oligocene	dark gray to greenish–gray shales with arenaceous intercalations	200–500 m	pelitic turbidites in thin layers	
					Epiligurian sequences
Montepiano Fm	lower Oligocene–middle Eocene	reddish shales with minor gray and blackish shales	50–300 m	hemipelagic deposits and pelitic turbidites in thin beds	
Varicoloured Shales	upper Cretaceous (Campanian–Cenomanian)	red, rose, black, greenish, brown and purple shales with siltite and sandstone intercalations	100–600 m	hemipelagic deposits and pelitic turbidites deeply tectonized and chaoticized	Basal Complex Ligurid II
Val Rossenna Shales (masses of Varicoloured Shales)	upper Cretaceous (Turonian–Cenomanian)	reddish and blackish shales with siltite intercalations	50–100 m	debris flows and mud flows in a sedimentary melange	Monghidoro
Variegated Shales	Cretaceous (Turonian–Albian)	red, purple, black and greenish shales with siltite and calcilutite intercalations	30–80 m	hemipelagic deposits and pelitic turbidites deeply tectonized and chaoticized	Basal Complex Ligurid I

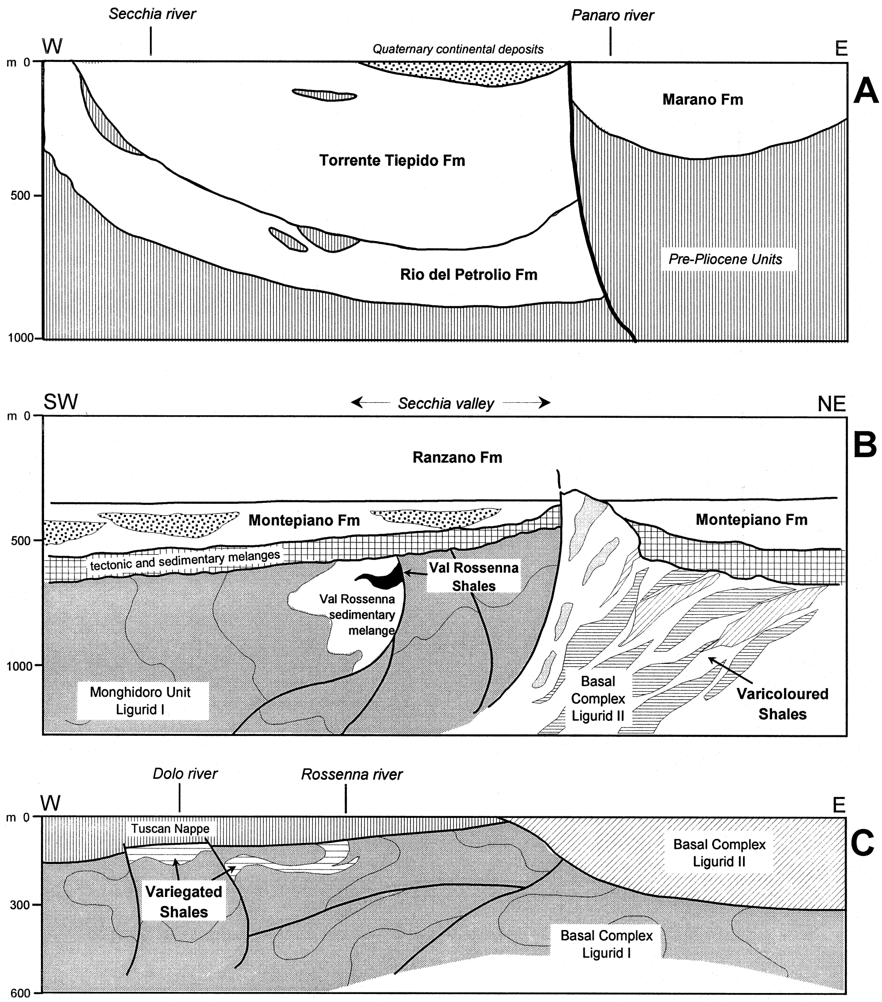


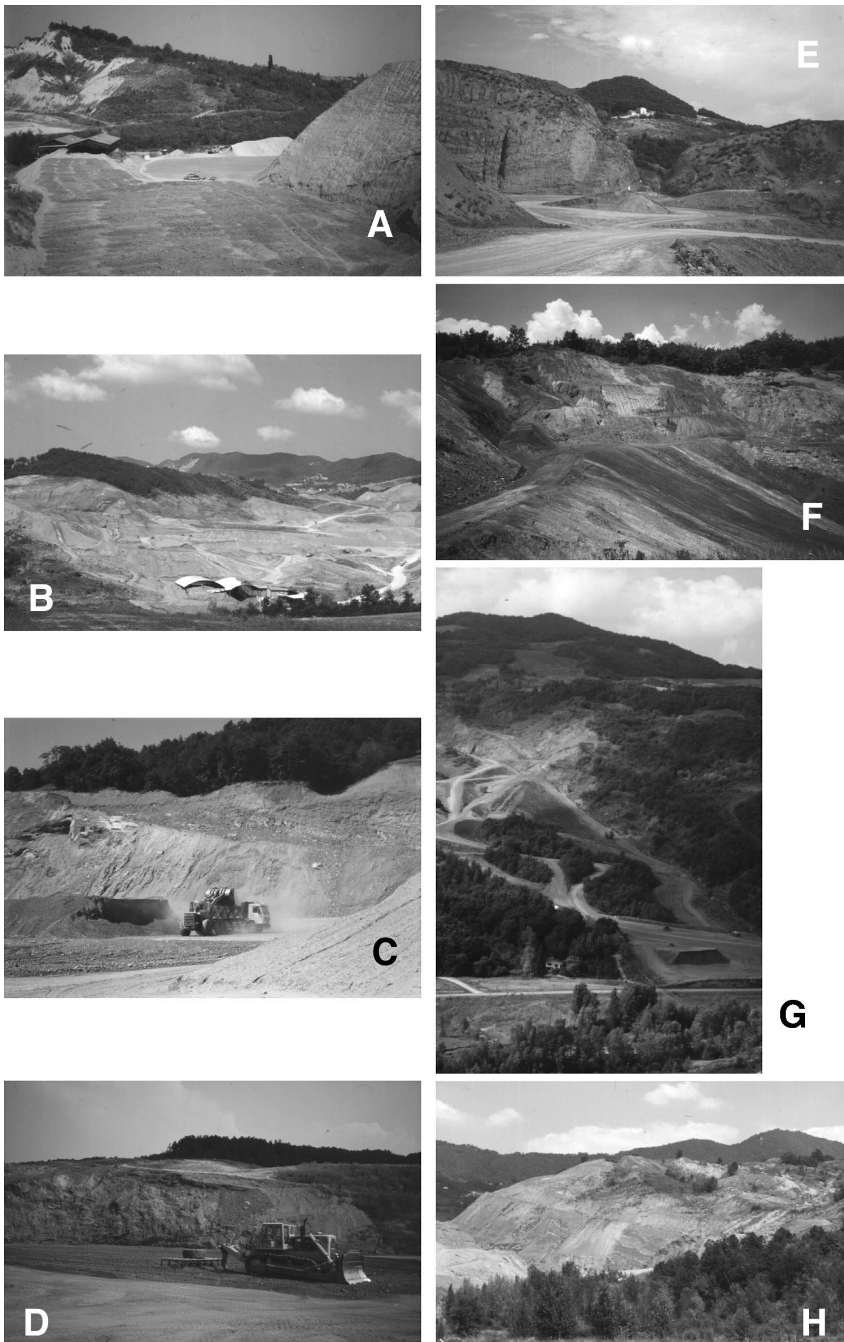
Fig. 2. Simplified geological sections through the northern Apennines around the Sassuolo Ceramic District (modified after Bettelli et al., 1987b; Gasperi et al., 1987). Structural relations of (A) Pliocene–lower Pleistocene blue-gray clays; (B) Varicoloured Shales, Val Rossenna Shales and Epi-Ligurian sequences (Montepiano Fm and Ranzano Fm); (C) Variegated Shales.

in the Baiso and Castellarano area (Fig. 3C). The mining of these shales is favoured by their considerable thicknesses (a few hundred metres) and by their fairly regular stratification, with inclinations between 20° and 60°.

The Montepiano Fm lies on Epiligurian sedimentary melanges and passes upward at the Ranzano Fm with a discontinuity of sedimentation. The Unit is characterised by two members which are lithologically very different from each other (Fig. 2B):

(a) reddish pelites in fairly regular sequences, several tens of metres thick, essentially located west of the Secchia River (Montepiano Shales, Fig. 3D).

(b) arkosic sandstones forming bodies several hundred metres thick, fundamentally diffused east of the Panaro River (Loiano Sandstones).



The Montepiano Shales constitute one of the traditional sources of clay materials of the Sassuolo District, with about ten active quarries situated mainly in the Secchia–Dorgola Basin. The principal mining problems are posed by lateral discontinuities of the deposits, due in large part to tectonic disturbances and rapid changes in the thickness of the Unit. Moreover, there are local intercalations of grey–green facies with a different composition with respect to the dominant reddish-coloured types.

A particular problem is posed by the selective mining of the Montepiano and Ranzano shales where the two Formations are in contact, especially where the former are of the same grey–green colour as the latter (Fig. 3E). In such cases the two lithotypes are frequently mixed, thereby obtaining raw materials with intermediate characteristics.

3.3. Ligurian units

The Ligurian nappes have been subjected to strong tectonic stress which has profoundly altered the original structure of the successions. In fact, the prevalently pelitic portions underwent ''plastic'' deformation, with almost complete chaoticization and transposition of the stratification along the cleavage (Basal Complexes). The calcareous and arenaceous units, on the other hand, maintained a ''rigid'' behaviour, forming tectonic shingles dispersed within the matrix of the Basal Complexes (Bettelli et al., 1987b).

In the area to the south of Sassuolo we recognise two overthrust nappes: Ligurid I (Basal Complex I and Monghidoro Unit) and Ligurid II (Basal Complex II and Cassio Unit). Outcrops of the former are within the apenninic chain, while the latter is found toward the margin with the Po plain.

The Basal Complex I is composed primarily of Palombini Shales (irregular bedding of shales and limestones) accompanied by Poggio Castellina and Ostia Sandstones and by minor bodies of Variegated Shales (Fig. 2C). These last-mentioned bodies have been occasionally used by the ceramic industry: they are deposits of modest size, with a maximum geometric thickness of 80 m (Fig. 3F).

The Monghidoro Unit essentially consists of the Monghidoro and Monte Venere Formations, which are devoid of any ceramic interest, to which, in Val Rossenna, a sedimentary melange is associated containing masses of Vari-

Fig. 3. Examples of clay deposits exploited in the Sassuolo District. (A) Torrente Tiepido Fm (Riola quarries). Epiligurian sequences: (B) Secchia–Dorgola Basin; (C) Ranzano shales, Varano de' Melegari Member (Pianella quarry); (D) Montepiano shales (L'Oca quarry); (E) selective mining of Ranzano (right) and (left) Montepiano shales (Ca' del Monte quarry). Ligurian Units: (F) Variegated Shales (Poggio Mezzature quarry); (G) Varicoloured Shales in the Val Rossenna sedimentary melange (La Caselletta quarry); (H) Varicoloured Shales in the Ligurid II (Roncobotto quarry).

coloured shales of moderate dimensions (Fig. 3G). Some of these masses have been mined, at times together with Lower–Middle Eocene reddish clays (Val Rossenna Shales).

The Basal Complex II is represented by a tectonic mix of Scabiazza Sandstones, Varicoloured Shales and Palombini Shales (Fig. 2B). The ceramic industry has in particular exploited the Varicoloured Shales, whose outcrops consist of bodies of considerable thickness in the lower Secchia and Panaro valleys (Fig. 3H). Today only two quarries remain active, due to objective mining difficulties connected with abrupt lithological variations (reflected in the different colour of the shales) and frequent passages to the Scabiazza Shales, with which the Varicoloured Shales were originally in lateral facies transition. It is also necessary to take into account the chaoticization, or in any case the strong variability of the inclination of the strata.

The Cassio Unit was not involved in mineral exploitation for the ceramic industry. Only a few quarries may have accidentally mined the Viano Shales (Paleocene–Middle Eocene), which lie west of Sassuolo at the base of the Montepiano Fm, in apparent continuity of sedimentation and with analogous lithological characteristics.

4. Compositional characteristics

Overall, the clays examined exhibit a rather wide spectrum of chemico-mineralogical compositions and grain size distributions. However, the individual geological units possess fairly uniform compositional characteristics, and therefore only the average values are reported (Table 2).

4.1. Plio–pleistocene grey–blue clays

The limited numbers of analyses available did not allow for significant differentiation in statistical terms, also because the analyses were referred to only six quarries (Bertolani et al., 1982; Neri, 1988; Venturi and Carrieri, 1994; Venturi, 1995). Therefore, the Torrente Tiepido, Marano and Rio del Petrolio Formations will be discussed jointly.

These are marly clays with 15–25% carbonates, represented essentially by calcite. Only in the Marano Fm dolomite is found in quantifiable amounts. The clay fraction is around 35–50% and consists fundamentally of illite and chlorite with scarce kaolinite and smectite occasionally present. The quartz-feldspathic component varies from 25 to 40% (Fig. 4). The Torrente Tiepido clays seem to be richer in phyllosilicates and poorer in quartz with respect to the other two units.

Table 2
Average chemical and mineralogical compositions of clay materials for ceramic tiles from the Sassuolo District, with standard deviation and number of data (n)

wt.%	Torrente Tiepido Fm ($n=4$)	Marano Fm ($n=3$)	Rio del Petrolio Fm ($n=4$)	Ranzano Fm		Montepiano Fm ($n=20$)	Varicoloured Shales ($n=7$)	Val Rossenna Shales ($n=4$)	Variegated Shales ($n=13$)
				marly ($n=27$)	low carbonates ($n=7$)				
SiO_2	47.9 ± 2.1	51.0 ± 2.4	50.6 ± 2.3	49.2 ± 3.2	56.9 ± 1.8	58.1 ± 2.0	56.1 ± 2.0	59.1 ± 2.8	57.8 ± 1.4
TiO_2	0.6 ± 0.0	0.6 ± 0.0	0.6 ± 0.0	0.6 ± 0.1	0.8 ± 0.0	0.8 ± 0.1	0.8 ± 0.1	0.9 ± 0.1	0.9 ± 0.0
Al_2O_3	13.4 ± 0.9	12.5 ± 0.6	13.4 ± 1.3	13.9 ± 1.4	16.8 ± 0.8	17.9 ± 0.7	18.4 ± 1.0	18.1 ± 0.9	20.8 ± 0.9
Fe_2O_3	5.3 ± 0.4	4.8 ± 0.3	5.0 ± 0.3	5.4 ± 0.6	6.8 ± 0.8	7.2 ± 1.2	7.6 ± 1.2	7.0 ± 0.6	7.9 ± 0.6
MgO	3.5 ± 0.6	3.3 ± 0.3	3.1 ± 0.4	3.4 ± 0.9	4.5 ± 1.0	3.0 ± 0.7	3.1 ± 0.8	2.7 ± 0.5	2.5 ± 0.3
CaO	11.3 ± 1.0	10.7 ± 1.4	10.7 ± 0.8	10.2 ± 2.5	2.2 ± 1.8	1.5 ± 1.5	1.9 ± 1.2	0.9 ± 0.8	0.2 ± 0.0
Na_2O	1.1 ± 0.3	1.3 ± 0.4	1.2 ± 0.1	1.3 ± 0.3	1.4 ± 0.4	1.3 ± 0.2	1.1 ± 0.2	1.4 ± 0.2	0.9 ± 0.3
K_2O	2.4 ± 0.1	2.3 ± 0.2	2.4 ± 0.2	2.6 ± 0.3	3.2 ± 0.1	3.3 ± 0.2	2.9 ± 0.3	3.6 ± 0.2	3.5 ± 0.3
L.o.I.	14.3 ± 0.9	13.2 ± 1.1	12.8 ± 0.9	12.8 ± 1.9	6.8 ± 1.1	6.6 ± 0.8	8.0 ± 1.3	5.8 ± 0.8	5.5 ± 0.6
Illite	24 ± 1	23 ± 2	23 ± 2	24 ± 2	31 ± 2	32 ± 2	30 ± 3	33 ± 1	37 ± 2
Chlorite	11 ± 2	6 ± 2	10 ± 1	9 ± 3	13 ± 3	8 ± 3	7 ± 1	7 ± 1	11 ± 1
Kaolinite	4 ± 1	3 ± 2	3 ± 1	3 ± 2	4 ± 4	4 ± 2	7 ± 2	4 ± 2	10 ± 2
Smectite	3 ± 5	traces	6 ± 4	5 ± 3	5 ± 1	6 ± 4	9 ± 4	8 ± 3	absent
Quartz	22 ± 3	29 ± 2	26 ± 4	23 ± 3	26 ± 4	28 ± 3	26 ± 3	28 ± 4	26 ± 3
Feldspars	10 ± 4	11 ± 3	9 ± 2	10 ± 4	12 ± 3	10 ± 3	7 ± 2	11 ± 3	8 ± 3
Calcite	20 ± 2	15 ± 3	19 ± 1	17 ± 5	3 ± 3	1 ± 1	traces	absent	absent
Dolomite	traces	8 ± 1	traces	3 ± 3	3 ± 3	4 ± 2	6 ± 5	2 ± 1	traces
Fe-oxides	4 ± 1	4 ± 1	3 ± 1	4 ± 1	5 ± 1	6 ± 1	6 ± 1	6 ± 1	6 ± 1
Accessories	2 ± 2	1 ± 1	2 ± 1	2 ± 1	1 ± 1	1 ± 1	1 ± 1	2 ± 2	2 ± 1

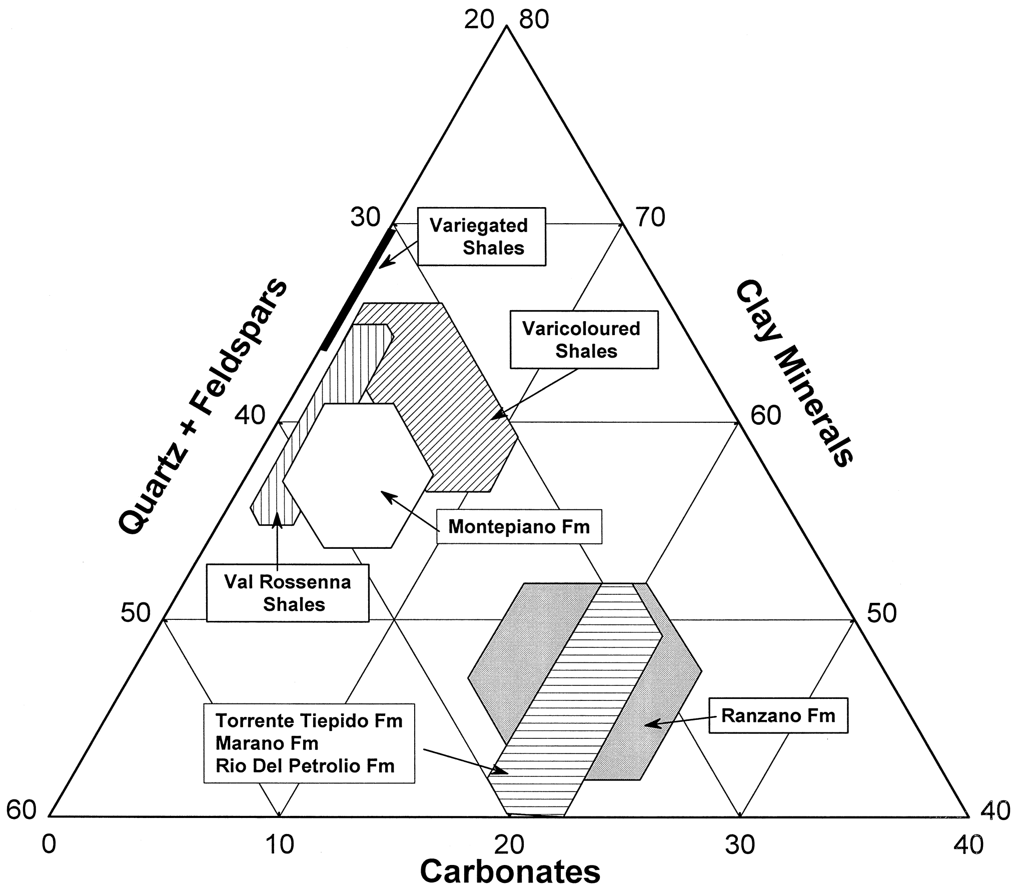


Fig. 4. Ternary diagram of the mineralogical composition of ceramic clays from the Sassuolo District. Fields represent average ± standard deviation of data.

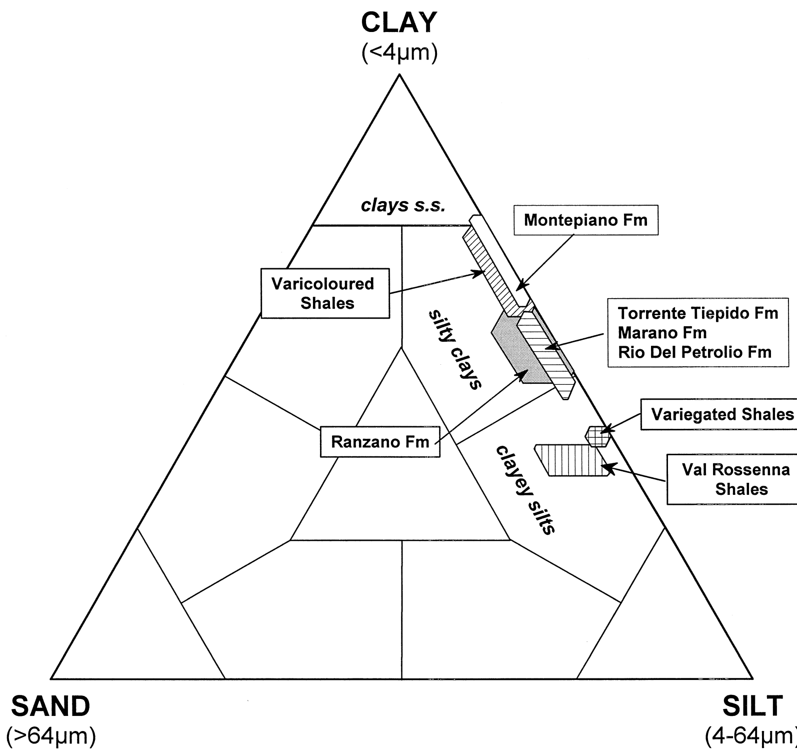


Fig. 5. Ternary diagram (Shepard, 1954) of the grain size distribution of clay materials from the Sassuolo District. Fields represent average ± standard deviation of data.

From the chemical standpoint, there are fairly homogeneous values of Al_2O_3 (12–15%), CaO (9–12%), Fe_2O_3 (4.5–6%), MgO (2.5–4%), K_2O (2–2.8%); silica is in the range of 46–54%. In terms of grain size distribution, they are in large part silty clays with few cases of clayey silts (Fig. 5).

4.2. Ranzano formation (Oligocene)

The numerous data available for this unit are referred to 16 quarries (Bertolani et al., 1982; Muratori and Venturi, 1983; Montermini et al., 1984; Venturi, 1986, 1995; Capelli and Bertolani, 1991; Venturi and Carrieri, 1994; Balestri et al., 1995) and reflect a markedly bimodal distribution of the chemico-mineralogical parameters, particularly with regard to the carbonate content. It was therefore necessary to distinguish between the prevailing lithotype, rich in carbonates and corresponding to the Varano de' Melegari Member, and a small population of samples poor in carbonates, presumably originating from the contact zone with the Montepiano Fm.

The classic Ranzano shales are characterised by the presence of calcite (12–22%) and dolomite (up to 7%) and by a significant quartz-feldspathic portion (28–38%). The clay fraction amounts to approximately 50% (Fig. 4) and is represented by illite and chlorite associated with smaller quantities of kaolinite and smectite; serpentine is also often present (Bolzan et al., 1983).

The chemical composition of the marly member is very similar to that of the Plio–Pleistocene grey–blue clays: SiO_2 (46–52%), Al_2O_3 (12–16%), Fe_2O_3 (5–6%), MgO (2.5–4.5%), CaO (7–13%), K_2O (2–3%). The grain size distribution is fairly homogeneous and permits their classification as silty clays (Fig. 5).

4.3. Montepiano formation (Eocene–Oligocene)

The analyses of the Montepiano shales reveal a remarkable compositional homogeneity, all the more significant because it is referred to a dozen different quarries (Bertolani et al., 1982; Venturi, 1986; Neri, 1988; Capelli and Bertolani, 1991; Venturi and Carrieri, 1994; Venturi, 1995).

There is a prevailing clay fraction (55–60%) which proves to be in large part composed of illite, with chlorite, smectite and kaolinite always present, albeit in smaller quantities. Carbonates are present in lower amounts, with dolomite predominating over calcite, while the quartz-feldspathic fraction is around 35–40% (Fig. 4).

The chemical composition is characterised by the following values: SiO_2 (56–60%), Al_2O_3 (17–18.5%), Fe_2O_3 (6–8.5%), MgO (2–4%), CaO (0–3%), K_2O (3–3.5%). The grain size distribution classifies the Montepiano shales as silty clays or, in some cases, as clays s.s. (Fig. 5).

4.4. Ligurian units (Cretaceous)

The available data for these materials are non-uniform, consisting of: a moderate number of results for the Variegated Shales which are however referred to a couple of localities (Bertolani et al., 1982; Bertolani et al., 1984; Bertolani and Loschi Ghittoni, 1983); a small group of samples of Val Rossenna Shales, coming from two quarries (Bertolani et al., 1982; Neri, 1988; Vignudini and Venturi, 1996); and finally seven analyses of Varicoloured Shales taken from six different quarries (Fabbri and Fiori, 1981; Bertolani et al., 1982; Venturi, 1995).

In all these units the phyllosilicate component is abundant (55–65%), particularly in the Varicoloured Shales where it reaches 65–70% (Fig. 4). Illite always predominates, associated with moderate levels of kaolinite and chlorite; smectite is present in significant amounts in the Varicoloured and Val Rossenna Shales but is absent in the Variegated Shales. Quartz is present in comparable quantities in the three units, while feldspars are more abundant in the Val Rossenna Shales. Carbonates are absent from the Variegated Shales, and consist essentially of dolomite in the other two units — fairly variable percentages in the Varicoloured Shales (0–12%) and traces in the Val Rossenna Shales.

The chemical compositions of the Cretaceous shales are fairly similar: SiO_2 (54–62%), Al_2O_3 (17–22%), Fe_2O_3 (6–9%), MgO (2–4%), CaO (0–3%), K_2O (2.5–4%). The greatest differences emerged in the grain size distribution (Fig. 5). In fact, the Varicoloured Shales prove to be very fine-grained and extensively overlap the Montepiano Fm in the field of silty clays. The Variegated Shales and Val Rossenna Shales, on the other hand, fall entirely into the field of clayey silts, notwithstanding their conspicuous phyllosilicate fraction. This is probably due to the presence in these units of micaceous terms having dimensions greater than 4 μm and/or of very tough clay fragments which are not dispersed by the usual treatments for sample preparation.

4.5. Comparison between the various clay materials

An overall comparison of the various units considered reveals certain clear differences in both the chemical composition and the clay mineralogy. For example, the amounts of carbonates, alumina or illite very clearly discriminate the marly materials (Ranzano, Torrente Tiepido, Marano and Rio del Petrolio Formations) from the red shales (Montepiano, Varicoloured, Val Rossenna and Variegated Shales). Quartz and feldspars on the other hand are present in fairly similar quantities in the various raw materials; the feldspathic component is moreover systematically represented by plagioclase with traces of K-feldspar.

More specifically, calcite predominates in the Plio–Pleistocene clays, while it is associated with dolomite in the Ranzano Fm (with an average ratio of 6:1); dolomite predominates in the red shales, although carbonates are entirely absent in the Variegated Shales. Further distinctions can also be made using the data for CaO, MgO and K_2O (Fig. 6) and those for chlorite, kaolinite and smectite (Fig. 7).

- The distribution of the Plio–Pleistocene grey–blue clays always overlaps the field of the Ranzano shales; the latter, however, exhibit a wider variability of data, especially for CaO and MgO.
- The group of carbonate-poor samples from the Ranzano Fm exhibits an intermediate composition between that of the Ranzano and Montepiano shales. The exception is an anomalous enrichment of MgO, linked to moderate contents of chlorite, dolomite and serpentine, which perhaps characterises certain levels of the succession where the two units are in contact.
- The Variegated Shales are also clearly distinguished from the other units by their higher content of alumina, potassium, illite, kaolinite and by the negligible quantity of calcium.

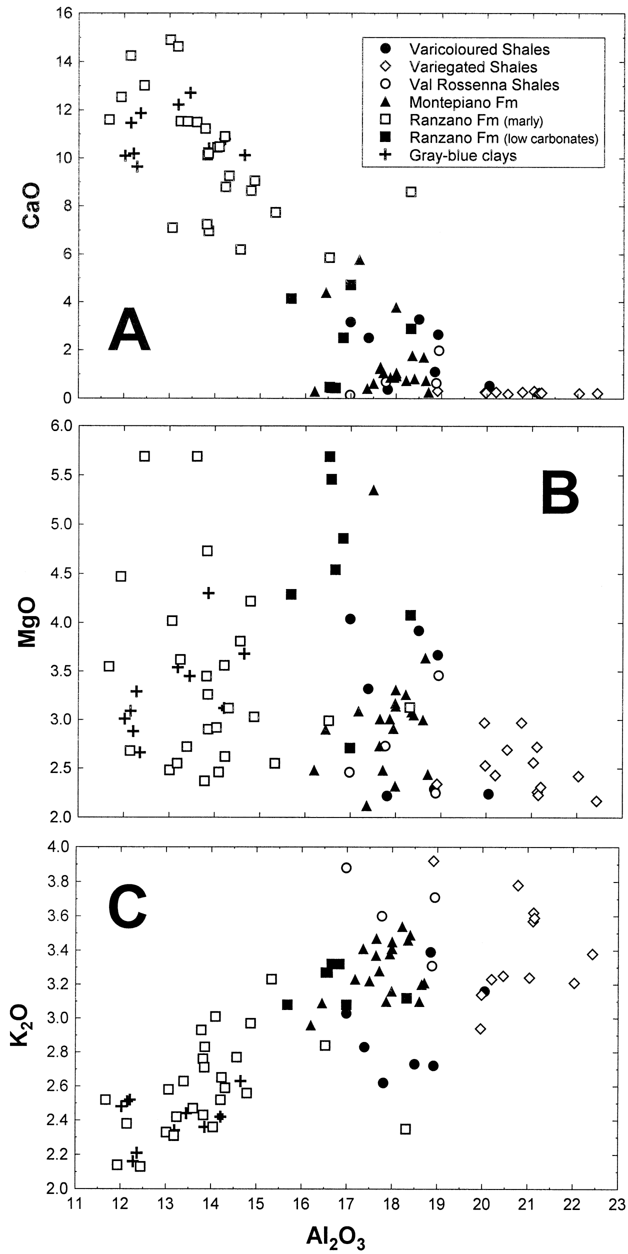


Fig. 6. Binary diagrams of the chemical composition of clay materials from the Sassuolo District. Correlation between alumina and CaO (A), MgO (B) or K_2O (C).

- The Montepiano Fm, the Varicoloured Shales and the Val Rossenna Shales have extensive compositional analogies (Fiori and Guarini, 1990). The Varicoloured Shales are principally differentiated by their generally higher

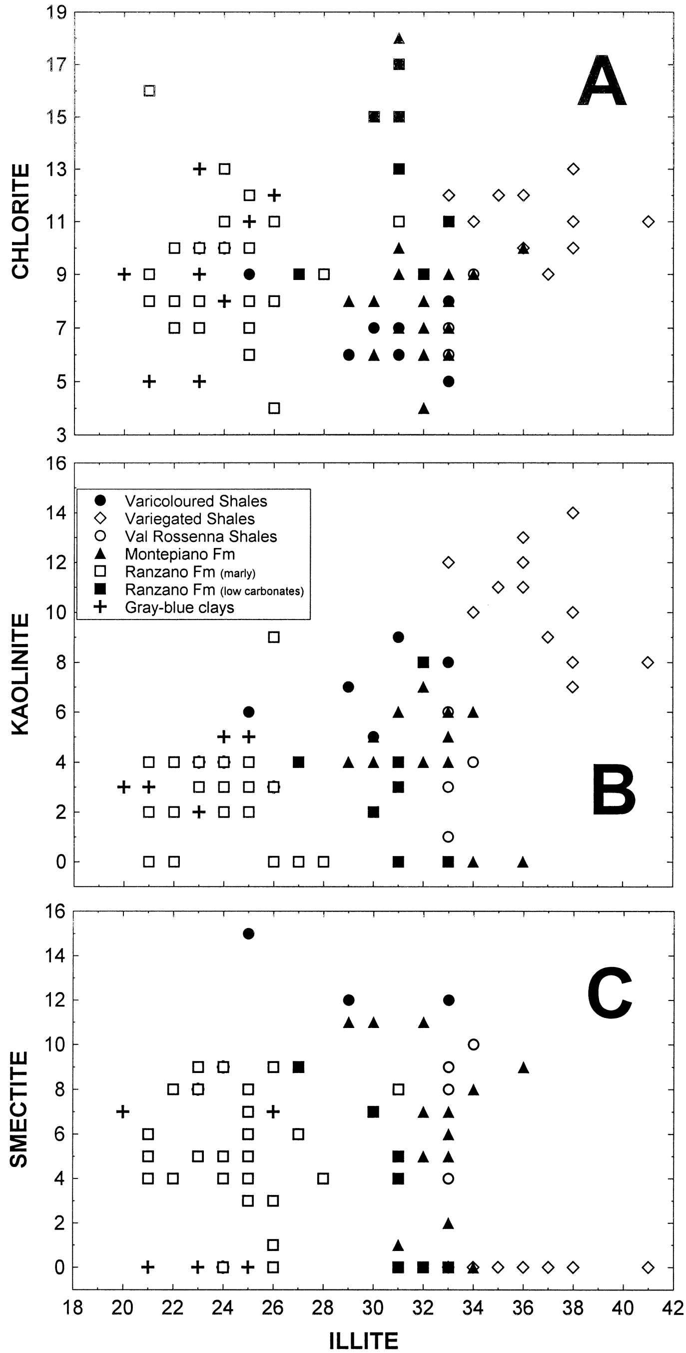


Fig. 7. Binary diagrams of the mineralogical composition of clay materials from the Sassuolo District.

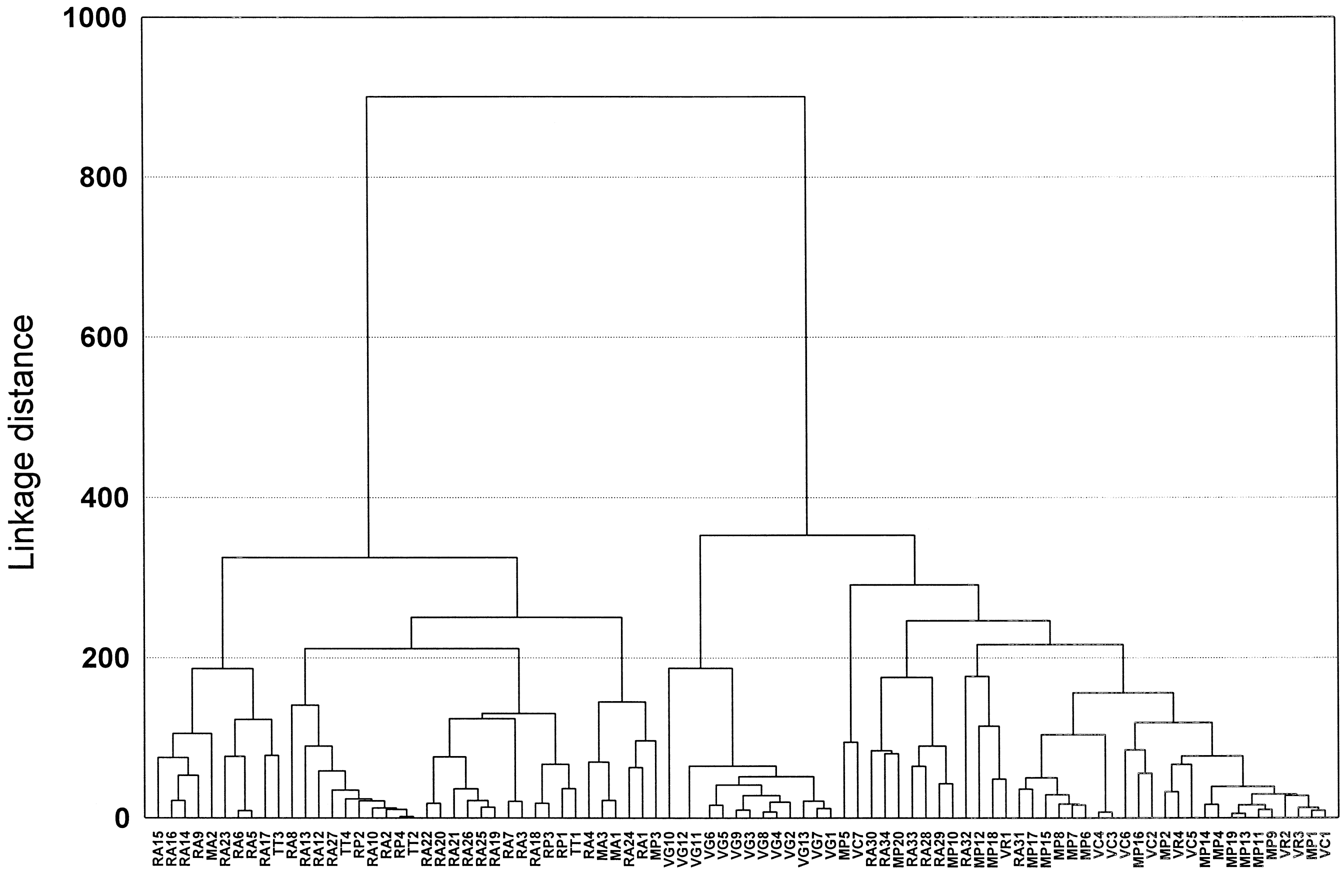


Fig. 8. Hierarchical tree plot for 88 clay samples based on all chemical and mineralogical variables. The tree clustering was performed using squared Euclidean distance as measure of dissimilarity and weighted pair-group average as linkage rule. TT: Torrente Tiepido Fm, MA: Marano Fm, RP: Rio del Petrolio Fm, RA: Ranzano Fm, MP: Montepiano Fm, VC: Varicoloured Shales, VR: Val Rossenna Shales, VG: Variegated Shales.

content of alkaline-earth elements, smectite and kaolinite, and by lower average values of silica, illite and K_2O. The Val Rossenna Shales differ from the Montepiano Fm primarily because they tend to be richer in potassium, as well as being coarser-grained.

These considerations are confirmed by multivariate statistical analysis of the chemical and mineralogical data (Fig. 8). In fact, in this tree-diagram the marly clays are clearly separated from the red shales; moreover, the Variegated Shales are clearly discriminated, as is the low-carbonate member (samples RA28–RA34) from the other samples of the Ranzano Fm.

5. Technological properties

The references for technological properties of the Sassuolo District clays are less numerous than the compositional ones, and are essentially restricted to evaluations of their plasticity (Bertolani et al., 1982; Cancelli et al., 1987; Vignudini and Venturi, 1996) and behaviour during the principal process phases: pressing, drying and firing (Venturi, 1981; Bertolani et al., 1982; Bertolani and Loschi Ghittoni, 1983; Muratori and Venturi, 1983; Montermini et al., 1984; Venturi, 1986; Neri, 1988; Capelli and Bertolani, 1991; Venturi and Carrieri, 1994; Balestri et al., 1995; Venturi, 1995; Vignudini and Venturi, 1996). These data must be interpreted with a certain degree of caution, because in most of the papers cited non-standardised methods and unspecified test conditions were employed. It is difficult to correlate the technological properties with the composition of the clays, because very few complete characterisations were carried out on the same sample; in fact, in many cases the technological and mineralogical data come from different samples for the same geological unit.

5.1. Plasticity of clay materials

As regards the Atterberg limits (Fig. 9 and Table 3), the most plastic materials tend to be the Montepiano shales, followed by the Varicoloured Shales. This is consistent with their fine grain size and significant smectite amount, which tends to raise the liquid limit and the plastic index. A lower plasticity is apparent in the Plio–Pleistocene clays and Ranzano shales, which are characterised by a coarser grain size and lower phyllosilicate content. Poor plasticity characterises the Variegated Shales, which are relatively coarse-grained and lack expandable clay minerals. The data for the Val Rossenna Shales is non-homogeneous and defines a vast field, probably due to varying quantities of smectite in the tested samples.

The methylene blue index is fairly consistent with the Atterberg data, in particular with the plastic limit (Table 3). The average MBI values range from

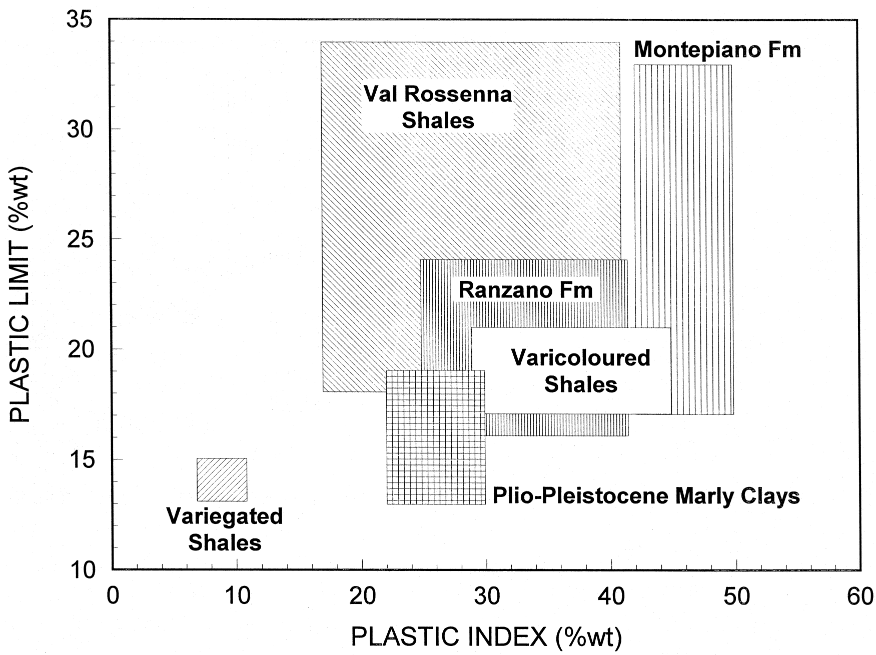


Fig. 9. Atterberg plastic index versus plastic limit of clay materials from the Sassuolo District.

25 meq/100 g for the Val Rossenna Shales to less than 10 meq/100 g for the Plio–Pleistocene clays.

5.2. Pressing and drying behaviour

The evaluation of the green and dry behaviour of the clays must take into account the absence of normalised tests, which in the literature has led to free variations of very important parameters such as the shape and size of the sample, the type of grinding (dry or wet), powder moisture, shaping pressure and drying curve.

In the cases studied, there is a predominance of dry grinding and medium-low values of powder moisture (4–6%) and shaping pressure (15–25 MPa); these conditions may justify the relatively low values shown in Table 3. In fact, the green bending strength is around 1 MPa while the dry bending strength is around 3 MPa for all the types of raw materials. The extremes are represented by the Montepiano and Ranzano shales, which is fairly consistent with the respective plasticity values. The data for the Plio–Pleistocene clays, on the other hand, are anomalously high with respect to the Atterberg limits and the MBI, and probably reflect different test conditions.

The pressing expansion is always low, except for the Ranzano shales which reach values of around 1 cm/m. The drying shrinkage is generally modest (0.2–0.3 cm/m).

Table 3
Average technological properties of clay materials for ceramic tiles from the Sassuolo District, with standard deviation and number of data (n)

	Unit	Blue–gray clays[a] ($n=8$)	Ranzano Fm ‘‘marly member’’ ($n=20$)	Montepiano Fm ($n=20$)	Varicolored Shales ($n=6$)	Val Rossenna Shales ($n=4$)	Variegated Shales ($n=1$)
Plastic Limit	wt.%	16 ± 3	20 ± 4	25 ± 8	19 ± 2	26 ± 8	14
Liquid Limit	wt.%	42 ± 1	52 ± 10	69 ± 6	57 ± 10	55 ± 4	23
Plastic Index	wt.%	26 ± 4	33 ± 8	46 ± 4	37 ± 8	29 ± 12	9
Methylene Blue Index	meq/100 g	6 ± 2	14 ± 4	23 ± 4	17 ± 5	25 ± 2	10
Pressing expansion	cm/m	0.4 ± 0.2	0.9 ± 0.3	0.6 ± 0.2	0.2 ± 0.1	0.4 ± 0.1	n.a.
Green bending strength	MPa	1.1 ± 0.3	0.9 ± 0.3	1.3 ± 0.2	1.1 ± 0.2	1.1 ± 0.1	n.a.
Drying shrinkage	cm/m	0.2 ± 0.1	0.3 ± 0.1	0.3 ± 0.1	0.2 ± 0.1	0.3 ± 0.1	n.a.
Dry bending strength	MPa	3.4 ± 0.9	2.7 ± 0.6	3.3 ± 1.0	3.0 ± 0.6	3.4 ± 0.3	n.a.
~1000°C							
Water absorption	wt.%	24 ± 2	20 ± 4	8 ± 5	13 ± 1	9 ± 1	n.a.
Firing shrinkage	cm/m	0.5 ± 0.5	1 ± 1	7 ± 3	2 ± 1	2 ± 1	n.a.
Fired bending strength	MPa	18 ± 5	14 ± 3	32 ± 7	15 ± 5	18 ± 4	n.a.
~1150°C							
Water absorption	wt.%	12 ± 7	15 ± 4	0.5 ± 0.5	4 ± 3	6 ± 2	<1
Firing shrinkage	cm/m	4 ± 3	3 ± 3	9 ± 2	7 ± 3	6 ± 2	8
Fired bending strength	MPa	40 ± 10	30 ± 5	42 ± 6	35 ± 5	30 ± 5	50

[a] Torrente Tiepido, Marano and Rio del Petrolio Formations. n.a. = not available.

5.3. Firing behaviour

Two maximum temperatures were taken into consideration: approximately 1000°C with traditional cycle (exemplified by majolica and ‘‘cottoforte’’) and approximately 1150°C with fast cycle (representative of ‘‘monoporosa’’ and red stoneware). It should be noted that the water absorption, linear shrinkage and bending strength values are always interdependent, and therefore the lower the water absorption, the greater the linear shrinkage and the bending strength will be (Table 3).

The data must be interpreted with a certain degree of caution, because the parameters measured on fired articles may vary rapidly within the thermal interval considered. Consequently, differences in firing temperature of a few tens of degrees may significantly modify the values of water absorption and those of the other variables. It should also be taken into account that the two temperatures chosen may not be the ‘‘optimal’’ ones for all the clays studied in the literature.

The firing of carbonate-rich materials (Plio–Pleistocene clays and Ranzano shales) produces at 1000°C highly porous articles (water absorption: 16–26%) with low shrinkage (< 2 cm/m) and relatively low bending strength (10–20 MPa). For the Montepiano Fm and the Variegated Shales, on the contrary, vitrification of the ceramic material is observed at 1150°C, with water absorption < 1% associated with high shrinkage (7–11 cm/m) and mechanical strength (30–50 MPa). In the case of Varicoloured Shales, on the other hand, we note the influence of the variable carbonate content which explains the non-uniform and fairly high values for water absorption at 1150°C (1–7%); the data for shrinkage (4–10 cm/m) and bending strength (30–40 MPa) are proportionally high and reflect the fine-grained nature of the clay material. The products obtained from Val Rossenna Shales are also not completely vitrified at 1150°C (4–8% of water absorption), due to the relatively coarse grain size of the raw material, which also entails lower values of shrinkage (4–8 cm/m) and bending strength (25–35 MPa) than those for the other red shales.

These firing behaviours can be compared with the technological requirements for ceramic tiles with coloured body (Fig. 10):

- the characteristics of fired Plio–Pleistocene grey–blue clays correspond well with those of majolica;
- the Ranzano shales are suitable for both majolica and ‘‘cottoforte’’, depending on their composition;
- the Variegated and the Montepiano Shales fully satisfy the requirements for unglazed red stoneware and can be introduced into complex bodies for glazed stoneware;
- the Varicoloured and Val Rossenna Shales do not easily attain the low porosity required by unglazed products, and are therefore better suited for glazed stoneware bodies;

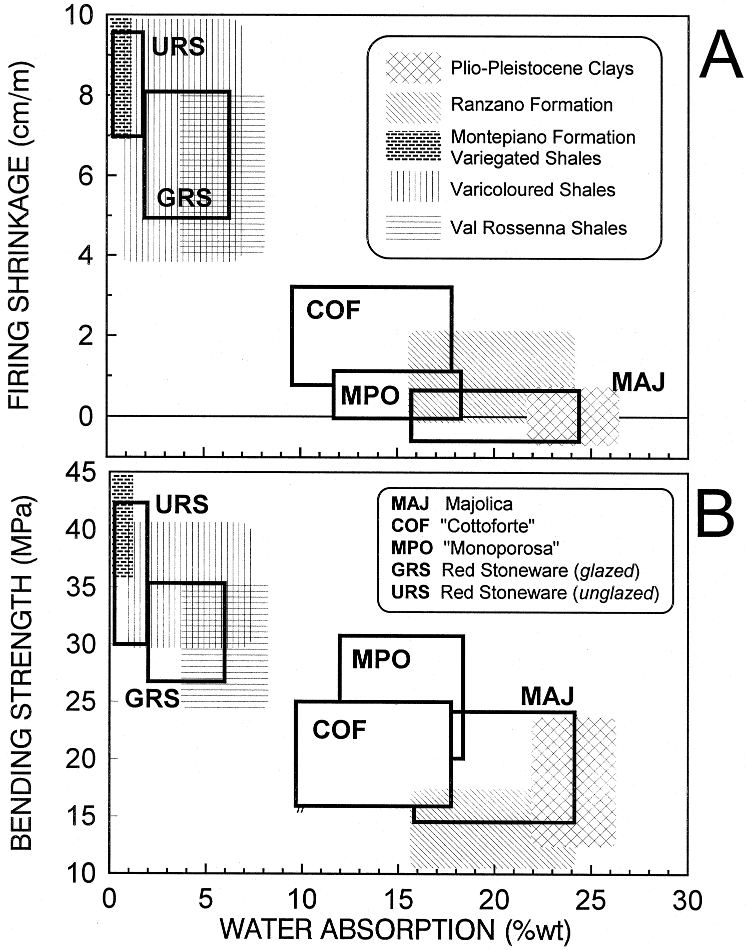


Fig. 10. Technological properties of the products obtained with clay materials from the Sassuolo District in comparison with the requirements of the various types of ceramic tiles. Water absorption versus firing shrinkage (A) and bending strength (B). MAJ: majolica, COF: ''cotto-forte'', MPO: ''monoporosa'', GRS: glazed red stoneware, URS: unglazed red stoneware.

- no natural raw material is able to satisfy the requirements for ''monoporosa'' on its own, and it has therefore become common practice to mix ''marly clays'', ''red shales'' and complementary materials.

6. Production and use of clay materials

The supply of clays for ceramic tiles in the Sassuolo District is assured at present by 26 quarries (Table 4). The applications are diversified as a function of the clay sources (Table 5).

Table 4
Production of clay materials in the Sassuolo Ceramic District

Geological unit	Number of quarries			Locality	Average output (tpa)
	1960–1998	Operating quarries in 1997–1998			
Torrente Tiepido Fm	22	2	Riola and Rio Riola	Fiorano Modenese	~ 100,000
Marano Fm	4	1	Buscadello	Vignola	~ 20,000
Rio del Petrolio Fm	9	1	La Rocca	Castellarano	~ 50,000
Ranzano Fm	21	7	Braglie and Molino Canavarola	Secchia–Dorgola Basin	~ 200,000
			Pianella and Castagneto	Tresinaro Valley	~ 100,000
			La Pianazza	Prignano sul Secchia	~ 50,000
			Querceto and Stadola	Castellarano	~ 250,000
Ranzano Fm +	13	6	Ca' del Monte and Ca' Talami	Baiso	~ 250,000
Montepiano Fm			Lovaro, Palladini, Poiatica and Montequercia	Secchia–Dorgola Basin	~ 350,000
Montepiano Fm	21	5	Boccadello, Boscaccio, Sopravigne and Vallo	Secchia–Dorgola Basin	~ 350,000
			L'Oca	Toano	~ 50,000
Varicoloured Shales	34	2	Badia	Monte S. Pietro	~ 100,000
			Roncobotto	Zocca	~ 100,000
Val Rossenna Shales	3	1	La Caselletta	Prignano sul Secchia	~ 50,000
Variegated Shales	3	1	Poggio Mezzature	Frassinoro	~ 30,000

Table 5
Use of clay materials from the Sassuolo District in ceramic tile manufacturing

Type of ceramic tile		Firing technology	Output 1997 (Mm^2)	Class ISO 13006	Clay materials		Complementary material	
Wall tiles	Majolica	traditional double firing	60	BIII	Gray–blue clays[a] Ranzano Fm	90–95%	5–10%	chamotte
	Birapida	fast double firing	20	BIII		85–90%	10–15%	chamotte, arkosic sand
	Monoporosa	fast single firing	32	BIII	Ranzano Fm Gray–blue clays[a]	40–60%	20–40%	arkosic sand, granite
					Montepiano Fm	20–30%		
Floor tiles	Cottoforte	traditional double firing	4	BII_b	Ranzano Fm	90–95%	5–10%	chamotte
	Red Stoneware (unglazed)	traditional single firing	4	BI_b	Montepiano Fm Varicoloured Shales Val Rossenna Shales	90–95%	5–10%	chamotte
	Red Stoneware (glazed)	fast single firing	63	BI_b BII_a	Montepiano Fm Varicoloured Shales Variegated Shales Val Rossenna Shales	70–80%	20–30%	basalt, gabbro, phonolite, arkosic sand, pumice, etc.

[a]Torrente Tiepido, Marano and Rio del Petrolio Formations.

The Torrente Tiepido and Rio del Petrolio Formations annually supply about 170,000 tons of marly clays, utilised in large part for the manufacture of majolica. The Marano Fm makes only a small contribution, because a large part of its production is taken up by a cement factory. Approximately 800,000 tpa are mined from the Ranzano Fm, and used for wall tiles and the modest residual production of ‘‘cottoforte’’. The approximately 700,000 tpa of red shales mined from the Montepiano Fm are used both for vitrified floor tiles and for ‘‘monoporosa’’. The applications of the Varicoloured Shales (∼ 200,000 tpa) and the Val Rossenna Shales (∼ 50,000 tpa) are in large part analogous to those of the Montepiano Fm, albeit more oriented toward red stoneware or in any case toward production with dry grinding. Finally, the Variegated Shales are occasionally used for glazed red stoneware (Bertolani, 1994).

This production scenario has radically changed during the past quarter century, with the abandonment of over 100 clay quarries for various reasons, such as the progressive introduction of ever-more restrictive environmental policies, imposing rigorous planning of mining activities.

A great impact has been made by innovative process technologies, such as fast firing and wet grinding with spray drying (Fig. 11B and C), which have led to drastic modifications in body design (Bertolani et al., 1986; Fabbri and Dondi, 1994). In fact, to overcome the problems typical of fast firing (‘‘black core’’ and ‘‘pinholes’’) the clay component of the bodies has been substantially reduced in favour of complementary materials (Table 5). Moreover, there has been a selection of clays whose rheological behaviour is better suited to wet grinding.

Another decisive factor has been the market variations, which have brought about the gradual decline of certain product types in favour of others (Fig. 11A), with dramatic repercussions on raw material procurement strategies within the Sassuolo District. In this regard, a case in point is the great commercial success of glazed light-coloured stoneware and porcelain stoneware, which have rapidly supplanted the traditional products with coloured body (red stoneware and ‘‘cottoforte’’). This has led to the large-scale use of imported white-firing clay materials, at the expense of Apennine clays which yield products of a reddish colour (Fabbri and Fiori, 1985; Fiori et al., 1989).

The production trends for the various clay materials of the Sassuolo District are shown in Fig. 11D, from which certain general points can be deduced.

- A significant reduction in the use of Plio–Pleistocene clays, principally due to the progressive decline of wall tiles, particularly majolica, and to the environmental restrictions imposed on the quarries, all of which operate near densely populated areas.
- Reduction in the use of Ligurian red shales due to a convergence of factors: strong decline of red stoneware, mining difficulties connected with the chaotic structure of the deposits, higher transport costs due to the greater distance of the quarries from Sassuolo, poor suitability for the wet grinding

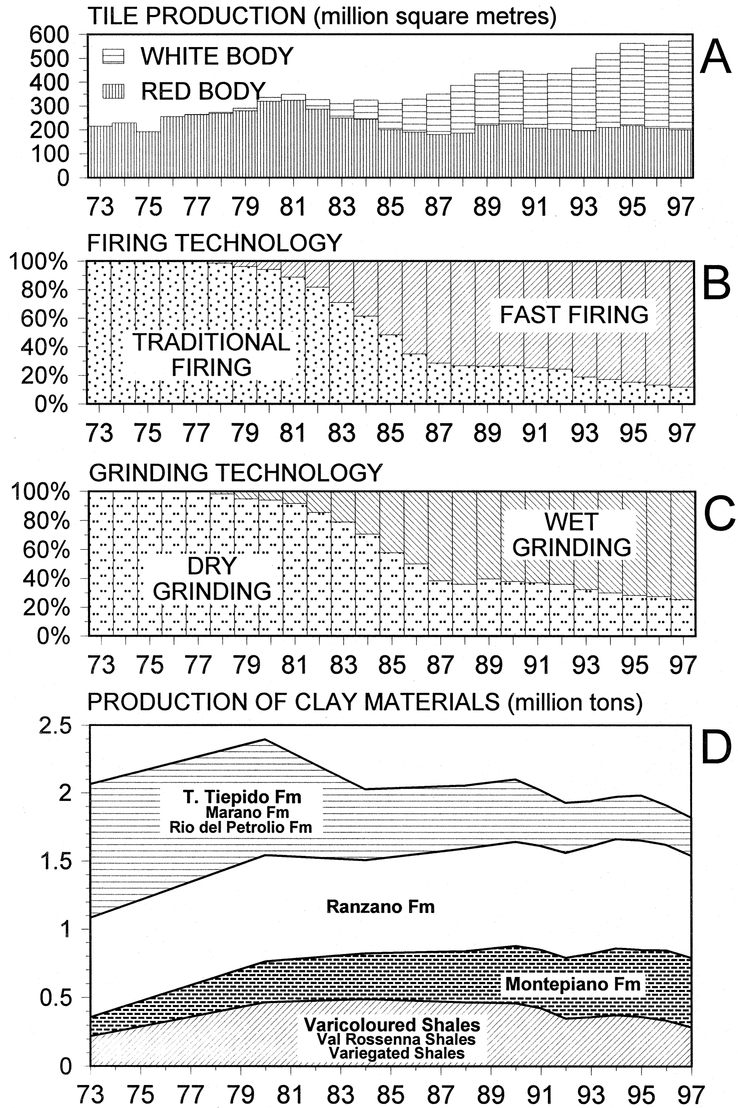


Fig. 11. Trends in ceramic tile production and technology in the period 1973–1997. (A) Italian tile production distinguished in white and red bodies; (B) ratio between traditional and fast firing; (C) ratio between dry and wet grinding; (D) production of clay materials from the Sassuolo District.

process, due to the presence of smectite, especially for Varicoloured Shales (Venturi, 1981, 1995).

- Substantial stability in the consumption of Ranzano and Montepiano shales, which have proved better suited to the new production processes than the other raw materials of the District. In fact, being used into the bodies for ‘‘monoporosa’’, ‘‘birapida’’ and glazed red stoneware, they have overcome without major consequences the disappearance of ‘‘cottoforte’’ and unglazed red stoneware. Moreover, the producers of these clays have been favoured by deposits of conspicuous size with a fairly regular structure and effective planning of mining activities (Colombetti, 1989; Bertolani, 1994).

7. Conclusions

In practice, the Sassuolo District has served over the past few decades as a large industrial scale laboratory for assessing the technological properties of clays and their suitability for the production processes of ceramic tiles.

The local clays, which in the past constituted the sole mineral resource of the District, now supply only 40% of the demand for clay materials. They are extracted from different geological units and distinguished in two principal types, with clearly differentiated composition and technological properties: ‘‘marly clays’’ and ‘‘red shales’’. Each year approximately 1 million tons of each of these types of clays are used in coloured bodies: marly clays for wall tiles (majolica, ‘‘birapida’’, ‘‘monoporosa’’) and red shales for both floor tiles (glazed red stoneware) and wall tiles (‘‘monoporosa’’). Traditional products such as ‘‘cottoforte’’ and unglazed red stoneware are in steep decline and have now all but disappeared from the market.

The sources of marly clays are the Ranzano Formation (Oligocene) and the Torrente Tiepido, Marano and Rio del Petrolio Formations (Plio–Pleistocene). These are all clays with a similar composition: 40–50% clay fraction, prevalently illite–chlorite, 15–25% carbonates and a significant silty portion (35–45%). The Ranzano shales exhibit a wider spectrum of composition and technological properties, which make them more suitable for the new production processes. In recent years they have progressively gained market share at the expense of Plio–Pleistocene clays, whose exploitation is increasingly penalised by the programming of mining activities imposed by their vicinity to the population centres of the Po Valley.

The sources of red shales consist of the Montepiano Formation (Eocene–Oligocene) and of some units of the Ligurian Complexes (Cretaceous), principally Varicoloured Shales. These raw materials exhibit substantial compositional analogies: 55–70% clay portion, with illite prevailing over chlorite, kaolinite and sometimes significant amounts of smectite; carbonates are low or absent; the silty fraction is less than 40% in the Montepiano Fm and in the Varicoloured Shales, while it amounts to 50–60% in the Variegated Shales and in the Val Rossenna Shales. Overall, these are generally plastic and fusible materials, especially the Montepiano shales whose consumption has gradually consolidated over the past decade, at the expense of the other red shales which have encountered growing obstacles in the mining of deposits, both due to their chaotic structure, and due to their greater distance from Sassuolo. The Varicoloured Shales, in particular, have shown many limitations in the wet grinding and fast firing phases, which have contributed to the closing of most of the quarries. The Val Rossenna and Variegated shales, on the other hand, have maintained a small market niche thanks to their peculiar compositional characteristics, especially the absence of carbonates and a prevalently silty grain size distribution.

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