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CHEMICAL, MINERALOGICAL AND TECHNICAL CHARACTERISTICS OF NATURAL CLAYS FROM MACEDONIA, N.GREECE AND THEIR EVALUATION FOR CERAMICS

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ABSTRACT

The suitability of natural clays from several areas of Macedonia, N.Greece, (Chalkidiki, Thessaloniki, Serres, Katerini, Giannitsa and Kilkis), for the production of earthenware (faience), semigres (cottoforte) and gres ceramic products, was investigated, by means of chemical, mineralogical and particle size analysis as well as of tests and measurements for specific gravity, pH, plasticity, fired water absorption, dried and fired shrinkage, and fired modulus of rupture. Most of the clays found to be suitable for earthenware and semigres ceramics as are the bricks and roof tiles, while some others found to be suitable for gres ceramics as are the low porosity (water absorption <4%wt) tiles and bricks.

INTRODUCTION

Natural clays are defined as, clays as they are actually found in the earth (Worrall, 1969). They contain in addition to the clay minerals and other minerals which affect the chemical, physical and technical characteristics of the clay substance.

Natural clays having specific properties are used for the production of earthenware (faience), semigres (cottoforte) and gres ceramics, as these products are described by the International Association for the Study of Clays (Veniale and Palmonari, 1974). On the basis of their water absorption (WA) these products are classified as, faience with 16-22 %wt WA, semigres with 12-19 % wt WA and gres with WA <4% wt. In the category of faience and semigres ceramics, are included, among other products, building bricks as well as roof and floor tiles while in the category of gres, the low porosity (<4% wt) tiles and bricks.

Natural clays that are used for building ceramic products (bricks, roof and floor tiles etc) and coarce earthenwares, are usually lean continental sediments, containing silt and fine sand while their clay fraction is less than 25% of the total material (Veniale and Palmonari, 1974). The value of such natural clays depends on their physical characteristics and on their chemical composition, the permissible range of which is very wide. The principal requirements for a clay used for building ceramic materials are; first, it must consist an extensive deposit accesible to large scale

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winning, second, it must be enough plastic in order to be shaped easily and retain its shape both in wet and dry state, third, it must vitrify sufficiently at a temperature between 950 and 1150 ^oC resulting to a hard ceramic material without deformation and excessive shrinkage (Grimshaw, 1971).

The clays which satisfy these requirements in a great extent are limited and although there are many which can be used quite satisfactory, it is wrong to assume that any deposit of clay can be used for making relevant building materials obeying to the required specifications.

The characteristics of natural clays for building ceramics are not easy defined since they have wide tolerances in their chemical and physical properties. Although the range of composition of natural clays is wide, there are certain requirements concerning their ingredients, in relation to their application.

Natural clays for building materials must contain, a certain proportion of clay minerals to develop the required plasticity, a proportion of filler materials as quartz or large fragments of feldspars to prevent excessive shrinkage on drying and firing and a proportion of fluxes as fine particles of alkali bearing minerals or some minerals containing magnesium, calcium or iron, acting also as fluxing materials above certain temperatures. Calcium compounds as limestone ($CaCO_3$) may provide disadvantages or advantages according to their particle size (Varsos and Sikalidis, 1993). Limestones, that are usually found in many Greek natural clays, produce on firing lime which slakes in moist air and may crack or "blow" the product (brick, roof or floor tile). This can be largely avoided by grinding the natural clay and consiquently the contained limestone to particles finner than 300 μm (Hollerl and Sikalidis, 1993). The finely divided CaCO3 provides advantages in iron rich clays improving on firing the dark red-brown colour of the product. Calcium compounds act also as binders by glass formation on firing, but in excess they cause premature fusion resulting to destortion of the product.

The need of technoeconomically accepted raw materials for manufacturers of building materials (bricks, roof and floor tiles etc) and other clay products, dictates the investigation, study and evaluation of local clays towards these applications.

Greek clays from certain areas of Chalkidiki (Alexiades, 1960 and 1968, Kaklamani and Anastasiadis, 1986), Attiki, Euboia, and Viotia (Mistardis, 1961, Perraki, 1987), and Krete (Perraki, 1990) have been studied concerning their application in ceramics and in other fields.

In the present work, the chemical, mineralogical and technical characteristics of natural clay samples from deposits of many areas of Macedonia, North Greece, (Chalkidiki, Thessaloniki, Serres, Katerini, Giannitsa and Kilkis), have been studied in order to determine their suitability for various products of the ceramics industry.

MATERIALS AND METHODS

Materials

One hundred and thirty clay samples were collected from the deposits of eight different locations shown on the map of N.Greece (Fig.1). The areas, the locations of sampling and their code letters used were: Chalkidiki (Ag.Panteleimon/CP), Thessaloniki (Langadas/TL and Chalkidona/TC), Serres (Skoutari/SS), Katerini(City/KC), Giannitsa (Kallipoli/GK and Palefito/GP) and Kilkis(Kristoni/KK). Data concerning the geological formations, where the studied deposits belong, are included in the relevant geological maps (IGME, 1983).

The samples from the area of Chalkidiki were collected from deposits of red Neogene clays, which are silty and occasionaly sandy, having a thickness of 200 m and in some positions even more. The deposits belong to the Post-Alpine sediments of the Circum Rodope belt.

The samples from the area of Thessaloniki were collected from Alluvial and Fluvio-lacustrine deposits of the Almopia belt. The samples from the area of Serres (specific interest shows the basin of Strimon river) were collected from Quaternary sedimentary deposits having grey to green colour and up to 3000 m thickness. These deposits consist of sandy clays, silt and sands. The samples from the area of Katerini were collected from Quaternary and Neogene sedimentary deposits which contain red clayey sandy materials, fine sand and loam. The deposits are in the boundary of Almopia and Pelagonian Zone. The samples from the area of Giannitsa were collected from the Alluvial and Fluvio-lacustrine sedimentary deposits of the Almopia belt in the boundary with the Paiko Zone. The samples from the area of Kilkis were collected from Quaternary sedimentary deposits of the Peonia Zone which contain red clays and red clayey sands with intercalations in some positions, of sand and gravel.

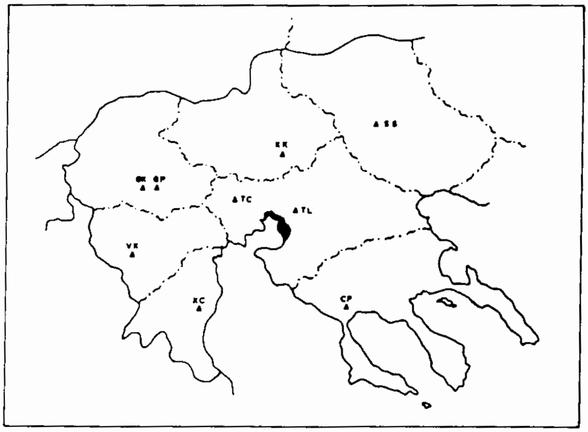

Fig. 1: Map of sample locations. CP: Chalkidiki (Ag. Panteleimon), TL: Thessaloniki (Langadas), TC: Thessaloniki (Chalkidona), SS: Serres (Skoutari), KC: Katerini (City), GK: Giannitsa (Kallipoli), GP: Giannitsa (Palefito) and KK: Kilkis (Kristoni).

Methods

The collected samples were sieved in a 4 mesh sieve and the residue on sieve was crushed in order to pass through the mentioned sieve. The total was thoroughly mixed and sufficient quantities were taken for the chemical and mineralogical analyses and the investigation of the technical characteristics. For the study of the samples the classical chemical analysis (Alexiades, 1980) and the techniques of X-ray Diffraction and Electron Microscopy were applied. The investigation of the technical characteristics of the samples, was carried out by means of tests and measurements according to the British Ceramic Society Testing Methods (1974, 1977), the English China Clays Ltd Testing Methods (1977) and the American Standards Testing Methods (1969). Specifically, particle size distribution, specific gravity, pH, plasticity, fired water absorption, wet, dry and fired shrinkage and fired modulus of rupture, were studied.

RESULTS AND DISCUSSION

The analytical data from ten promising samples representative of the studied deposits are given in Tables 1 and 2.

The evaluation of the studied samples concerning their suitability for ceramic products, namely faience (earthenware), semigres (cottoforte) and gres, on the basis of their chemical composition and in accordance to Vincenzini and Fiori (1977) diagramms, is illustrated in Figure 2.

The samples can be classified in three groups.

Table 1: Chemical analyses of samples CP11, CP22, CP31, TL2 and TC4 from the studied natural clay deposits

Oxides %wt	Samples CP11	CP22	CP31	TL2	TC4
SiO_2	66.25	62.40	57.47	61.92	57.23
Al_2O_3	14.02	15.20	9.15	15.56	14.28
Fe_2O_3	5.90	5.97	5.64	6.15	5.77
CaO	1.40	1.86	6.94	2.93	5.94
MgO	2.02	1.97	6.70	2.37	2.97
k_2O	2.27	2.64	1.20	2.89	2.14
Na_2O	1.45	2.15	1.06	2.31	1.99
TiO_2	0.62	1.53	0.48	0.50	0.64
MnO_2	0.09	0.11	0.12	0.08	1.12
SO_3	0.18	0.09	0.19	0.11	0.16
LOI	5.80	6.07	11.05	5.18	7.76

Table 2: Chemical analyses of representative samples KC6, GK5, GP7, KK4 and SS3 from the studied natural clay deposits

Oxides % wt	Samples KC6	GK5	GP7	KK4	SS3
SiO_2	65.47	50.49	50.70	62.40	59.90
Al_2O_3	12.33	12.48	13.04	14.87	16.06
Fe_2O_3	5.12	6.49	7.43	7.15	6.58
CaO	3.48	7.97	6.48	1.21	2.72
MgO	1.86	6.42	7.06	2.87	2.32
K_2O	2.03	2.83	2.41	2.54	3.60
Na_2O	1.76	1.33	1.05	0.84	2.36
TiO_2	1.00	0.33	0.50	0.83	0.83
MnO_2	0.09	0.13	0.15	0.17	0.10
LOI	6.86	11.53	11.18	7.10	5.52

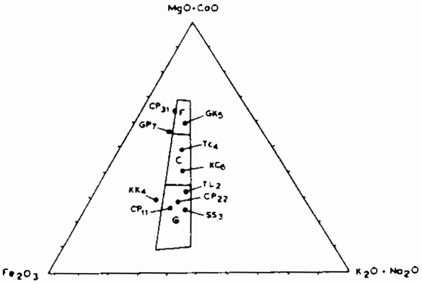

Fig. 2: Evaluation of the samples on the basis of their chemical composition. F:Faiance (earthenware), C:Cottoforte (semigres), G:Gres.

Table 3: Semiquantitative mineralogical analyses of the samples CP11, CP22, CP31, TL2, TC4, KC6, GK5, GP7, KK4 and SS3

	Minerals Present								
Sample	Mo	Cl	Il+Mi	Talc	Amf	Q	F	Dol	Cal
CP11	*	*	**			***	***		Tr
CP22	*	*	**			***	***		Tr
CP31			**			****	**		**
TL2		**	****		Tr	***	**		
TC4		**	****		Tr	**	**		*
KC6		*	*			*****	**		*
GK5		***	***	Tr	*	*	*	*	*
GP7	*	***	**	*	Tr	*	**	*	*
KK4		*	****			*****	*		
SS3		**	***		Tr	***	***		

* = 1-10 %wt, ** = 10-20 %wt, *** = 20-30 %wt etc, Tr = Traces
Mo=Montmorillonite, Cl=Chlorite, Il=Illite, Mi=Mica,
Amf=Amphiboles, Q=Quartz, F=Feldspar, Dol=Dolomite, Cal=Calcite

In the first group are included the samples GK5 and CP31 found to be suitable for faience (earthenware) (Fig. 2) which are products with comparatively high values of apparent porosity. The high amounts of carbonates, 14.23 and 13.28% wt, determined for GK5 and CP31, respectively, have as result high values of apparent porosity after firing due to the carbonates decomposition (starting at about 750 ^{o}C) and the volatilization of CO_2.

This is in accordance to the high values of fired water absorption and the relatively low values of fired modulus of rupture determined for the two samples, as is indicated in Tables 4 and 5. The values of water absorption start reducing rapidly from firing temperatures above 1050^{o}C (Fig. 4), indicating that reactions among the components has started resulting to sintering and high shrinkage values (Fig. 4, and Tables 4 and 5). The sample GP7 is out of the limits for faience ceramics (Fig. 2). This sample although it has similar chemical characteristics shows some notisable differences. Its carbonates content (11.4 %wt) is lower to that of GK5 (14.28 %wt) and furthermore it contains talc (Table 3). Dehydration of talc (at about 1000 ^{o}C) yields products as protoenstatite and amorphous silica which reacting with other constituents, assist softening and sintering resulting, comparatively to samples GK5 and CP31 to lower values of water absorption and higher values of mechanical strength (Tables 4 and 5) (Ford, 1967). These values are also favoured by the high percentage of the smallest particles (24.2%wt<3 μm).

In the second group are included the samples TC4 and KC6 which on the basis of their chemical analysis (Fig. 2) are suitable for semigres (cottoforte) ceramics. The carbonates content determined for both samples (10.60 and 6.20 %wt, respectively) found to be lower than the samples GK5, CP11 and GP7. This favoures lower values of water absorption after firing, if the sintering process has been developed and the product has been matured. This has not happened in the case of TC4, as it is suggested from the water absorption values for specimen fired at 950 to 1150 oC, which does not show serious difference (Table 4). This is also supported from the low modulus of rupture values (Table 4). These results indicate that TC4

Table 4: Technical characteristics of the samples CP11, CP22, CP31, TL2 and TC4 fr
the studied natural clay deposits

Technical characteristics*	Samples				
	CP11	CP22	CP31	TL2	TC4
Specific Gravity	2.67	2.68	2.63	2.53	2.60
pH	8.9	9.1	9.3	8.5	8.7
Plasticity	31.6	25.2	26.2	25.3	27.6
Water Absorption					
Fired at 950°	14.8	15.8	22.5	21.6	24.1
1050°	11.2	14.5	22.4	20.5	23.8
1150°	0.8	0.9	12.4	18.9	22.4
Shrinkage					
Wet to Dry	9.4	7.6	6.1	4.8	4.9
Dry to Fired at					
950°	10.7	7.5	6.8	5.2	4.8
1050°	13.4	8.8	7.1	4.0	4.6
1150°	16.5	13.1	11.7	6.3	5.0
Modulus of Rupture					
Fired at 950°	210.2	206.4	110.5	62.3	79.8
1050°	225.4	220.1	125.8	65.7	82.2
1150°	384.2	366.8	131.2	78.2	94.2
Particle size					
-4000 +250	19.1	20.0	35.0	14.1	3.5
-250 +88	16.1	14.2	16.4	22.8	14.8
-88 +63	4.2	6.2	5.9	5.4	7.9
-63 +3	35.8	38.0	30.4	46.8	62.3
-3	24.8	21.6	12.3	10.9	11.1
Natural colour	Red	Red	Red	Grey	Grey

* Specific Gravity in g/cm^3, Plasticity in ml H_2O/100 g, Water Absorption in wt %, Shrinkage linear in %,
Modulus of Rupture in kgf/cm^2, Particle size in μm and in wt %.

sample needs higher peak temperatures to be fired and/or more extented firing schedules in order to become sintered and matured and to develop the required properties for semigres products (Veniale and Palmonari, 1974). The sample KC6 has comparatively lower content of carbonates (6.2 %wt) but higher quartz content (Table 3). The water absorption values as well as the modulus of rupture values determined (Table 5), found to be within the limits for semigres ceramics (12-19 %wt water absorptio and 70-190 kgf/cm^2 modulus of rupture) (Veniale and Palmonari, 1974).

In the third group are included the samples CP11, CP22, TL2 and SS3, which on the basis of their chemical analysis (Fig. 2) are suitable for gres ceramics. The samples CP11 and CP22 have similar mineralogical analysis (Table 3) and similar particle size distribution (Table 4). The particle size distribution and the minerals present in certain particles fractions (Fig. 3) are suitable for gres ceramics. In addition, the determined water absorption values for the samples CP11 and CP22 fired at 1150 oC was 0.8 and 0.9 %wt respectively and their modulus of rupture values 384.2 and 366.8 kgf/cm2, indicating their suitability for gres ceramics (e.g. water absorption values < 4 %wt and modulus of rupture values 250-450 kgf/cm2)

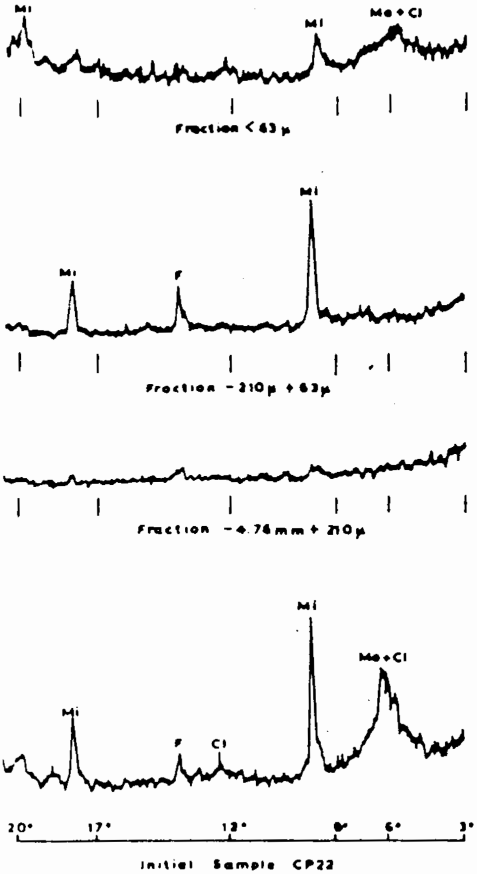

Fig. 3: X-Ray Diffractogramms (3 to 20^{o}) indicating the variations of clay minerals presence in the sample CP22 and its fractions. Mo=Montmorillonite, Cl=Chlorite, Mi=Mica, F=Feldspar.

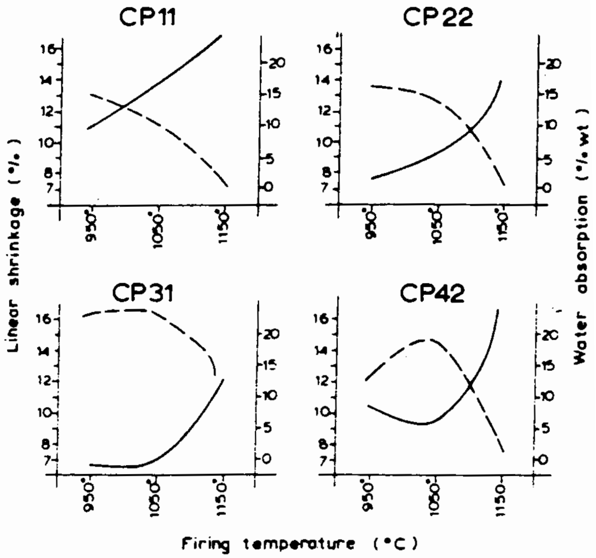

Fig. 4: Linear shrinkage (—) and Water absorption (---) vs Firing temperature for the samples CP11, CP22, CP31 and CP42.

(Veniale and Palmonari, 1974, Singer and Singer, 1978). Furthermore the gradual reduction of water absorption and linear shrinkage values (Fig. 4) of these samples support the fact that no deformation and premature fusion was observed. The samples TL2 and SS3 contain high percentage of Illite, Mica and Chlorite (Table 3) and their water absorption values even when fired at 1150 ^{o}C are high, 18.9 and 10.8 respectively. Also their modulus of rupture values (Tables 4 and 5) are low, especially for the sample TL2 (78.2 kgf/cm^2 at 1150 ^{o}C). These results suggest that the samples TL2 and SS3 need to be fired at higher temperatures and/or longer firing schedules in order to become sintered and matured and to develop the required properties for gres products (Veniale and Palmonari, 1974).

The sample KK4 found to be out of the limits for gres ceramics (Fig. 2), showing high water absorption value 15.1 %wt and low modulus of rupture value 81.3 kgf/cm^2 even when fired at 1150 ^{o}C (Table 5) indicating higher refractoriness due to his high content of quartz, mica and illite.

Finally all the samples excibit acceptable plasticity values.

CONCLUSIONS

The natural clays from the studied deposits of Macedonia (N.Greece) were found to be suitable for various industrial ceramic applications. The

Table 5: Technical characteristics of the samples KC6, GK5, GP7, KK4 and SS3 from the studied natural clay deposits

Technical characteristics*	KC6	GK5	GP7	KK4	SS3
Specific Gravity	2.63	2.61	2.58	2.65	2.58
pH	8.6	8.7	8.5	8.7	8.9
Plasticity	25.8	28.0	33.0	32.0	26.8
Water Absorption					
Fired at 950°	19.1	26.0	17.2	18.1	15.9
1050°	18.4	24.3	15.4	18.0	13.7
1150°	14.6	23.9	15.1	15.1	10.8
Shrinkage					
Wet to Dry	7.8	6.2	10.1	5.9	8.2
Dry to Fired at					
950°	8.3	6.0	10.7	6.1	8.5
1050°	8.1	6.1	11.8	6.4	10.2
1150°	8.4	7.1	12.1	10.9	10.5
Modulus of Rupture					
Fired at 950°	128.6	103.5	219.1	64.4	164.3
1050°	137.1	117.1	220.1	71.4	173.6
1150°	153.2	119.5	210.2	81.3	199.5
Particle size					
-4000 +250	22.7	5.0	7.6	26.4	3.6
-250 +88	12.6	3.8	2.8	22.7	7.8
-88 +63	4.9	2.9	2.4	6.9	6.3
-63 +3	47.0	72.8	62.3	30.5	64.9
-3	13.2	15.2	24.2	13.2	17.4
Natural colour	Grey	Grey	Grey	Red	Grey

* Specific Gravity in g/cm^3, Plasticity in ml H_2O/100 g, Water Absorption in wt %, Shrinkage linear in %, Modulus of Rupture in kgf/cm^2, Particle size in ìm and in wt %.

natural clays from Chalkidiki (Ag. Panteleimon), were found to be suitable for use in the production of bricks, roof tiles and coarse earthenware tiles. Also samples from other locations of the same area were found to be suitable for gres ceramics as are the low porosity (<4 %wt water absorption) ceramic products. The clay samples from Palefito, (Giannitsa), were found to be suitable for bricks and roof tiles and with mixing together with clays from Kalipoli could upgrade the properties of these products. The clays from Langadas and Chalkidona (Thessaloniki), were found to give fired ceramic products with high water absorption and low mechanical strength values, suggesting the need of mixing with other easier to be vitrified clays. The clays from Katerini, Kilkis and Serres were found to be suitable for bricks, roof tiles and coarse earthenware. In general, clays even from the same deposit but from different location may excibit occasionally variations that differentiate them and govern their use. Furthermore, it must be emphasized that conclusions based only on chemical characteristics may leed to misjudgement concerning the suitability of clays for ceramic applications and that mineralogical and mainly technical characteristics are necessary for correct and solid conclusions.

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