Metallurgy and materials

Metalurgia e materiais

The Tatuí Formation as a source of raw material in the ceramic pole of Santa Gertrudes (SP)

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Murilo Zaine Curtolo[1,2]
https://orcid.org/0000-0002-8827-0608
Cibele Carolina Montibeller[1,3]
https://orcid.org/0000-0002-4333-2115
Guillermo Rafael Beltran Navarro[1,4]
https://orcid.org/0000-0002-9717-4589

[1]Universidade Estadual Paulista "Júlio de Mesquita Filho, Geociências e Meio – Ambiente, Rio Claro - São Paulo - Brasil.

E-mails: [2]muri-lo-zaine@hotmail.com, [3]cibele.cm@outlook.com, [4]guillermo.navarro@unesp.br

Abstract

The importance of the Santa Gertrudes Ceramic Complex (SGCC) in the ceramic market is directly associated with the high quality of the Corumbataí Formation clays used in the manufacture of its products. Although the volumetric capacity of the Corumbataí Formation is able to meet the SGCC demand for the coming years, its industries are always in search of alternative sources for raw material, among these sources is the Tatuí Formation. In order to determine if the sediments coming from the Tatuí Formation have the potential to be used in the ceramist industry, geochemical, mineralogical and physical characterization tests were carried out on samples obtained from two different profiles. The analyses showed a sequence of fine sandstones rich in SiO_2 and Al_2O_3, with a mineralogy composed of quartz, potassium feldspar / plagioclase (albite), filosilicates and iron oxides in secondary proportions. The ceramic tests, in turn, presented heterogeneous results for the specimens submitted to burning at 1150 º C, but in general, the material coming from the Tatuí Formation has a promising potential within the field of ceramic manufacturing.

Keywords: Tatuí Formation, ceramic, raw materials, geochemistry, mineralogy.

1. Introduction

Currently considered to be the main center for the production of ceramics in Latin America, the Santa Gertrudes Ceramic Complex (PCSG) comprises about 30% of the national exports of ceramic products and is responsible for profiting over R$ 26 million in the first half of 2016. Such profit is associated mainly with the exports of products such as floors, tiles and porcelain tiles. The PCSG's highlight in both domestic and international markets is directly associated to the quality of the raw materials used in the manufacture of its products. This raw material is comprised of mostly clays from the Corumbataí Formation (Permian) (Christofoletti and Moreno, 2011; Rocha, 2012).

Although the reserves of the Corumbataí Formation are capable of supplying the PCSG's demand for raw materials for the next few decades, the search for new sources of these kinds of material has always been a concern for its industries. Among these possible sources are the sediments coming from the Tatuí Formation, a Permian sedimentary unit characterized by a fine-grained to medium sandstone package associated with the post-glacial phase of the Paraná Basin in the state of São Paulo (Rochas-Campos, 1967; Landim, 1970).

Despite being the subject of many scientific articles in the last decades (Soares, 1972; Steveaux, 1986; Assine, Zacharias and Perinotto, 1999; Barbosa-Gimenez, Caetano-Chang, 2010), so far the Tatuí Formation has only been characterized by its stratigraphic, sedimentary and paleontological aspects, leaving aside its geochemical, petrographic and economic features. The main goal of the present study is to determine if the sediments of the Tatuí Formation can be applied as an alternative source of raw materials for PCSG by applying the parameters and techniques used in the industries of the region.

1.1 Study area

The PCSG is located in the center-west portion of the state of São Paulo and comprises the areas of Rio Claro (SP), Cordeirópolis (SP), Ipeúna (SP), Limeira (SP), Piracicaba (SP) and Santa Gertrudes (SP) cities. The study region is served by several highways, with the Washington Luiz highway (SP-310) being the main one, located in the macrogregion of the municipalities of Rio Claro and Piracicaba, about 200 km from the capital of the State of São Paulo. The study area is located about 15 km from the center of Rio Claro, between the Fausto Santo Mauro and Irineu Penteado highways, and covers portions of the municipalities of Rio Claro and Ipeúna within the topographic sheet of Rio Claro (Figure 1).

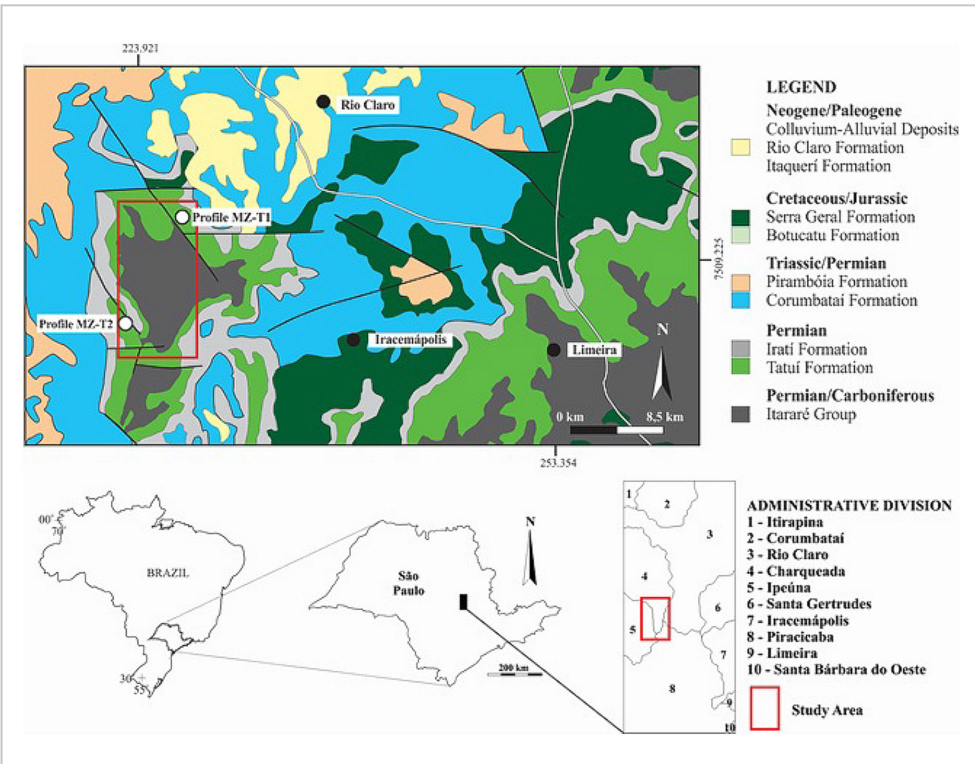

Figure 1 - Map of the location of the study area highlighting the profiles studied (MZ-T1 and MZ-T2). Source: Author.

2. Materials and methods

The methodology applied in the characterization of the nine samples from the Tatuí Formation followed the model used by the PCSG industries during the manufacturing process of their products and applied in the studies of Motta, Zanardo and Cabral Junior (2001), Rocha (2012) and Montibeller (2015) as well. The characterization process integrated data referring to samples gathered from two distinguished profiles (MZ-T1 and MZ-T2) from the Tatuí Formation located in the region of Ipeúna (SP) and Paraisolândia district (SP). Sample classification will follow the nomenclature established in ABNT NBR 13817:1997 (ABNT, 1997b).

3. Results

3.1 Geochemical and mineralogical analysis

The lithiogeochemical tests showed that the thirteen samples are constituted mainly by SiO2 (60.07% - 75.23%), Al_2O_3 (10.09% - 17.17%) and Fe_2O_3 (1.46% - 3.91%) (Table 1). The low CaO contents are directly associated with the $CaCO_3$s content of the samples (0.07% - 0.77%). These concentrations are related to its mineralogy, which is composed mainly of quartz (± 50%), plagioclase (albite?) / potassium feldspar (FK) (± 30%), iron oxides (± 12%) and phyllosilicates (± 8%); this mineralogical composition is supported by the petrography analysis (Figure 2) and diffractograms generated by the analysis of the total rock. Petrography also revealed that the lithotypes of both profiles correspond to fine sandstones.

Table 1 - Content of main oxides per sample.

Sample	SiO_2 %	Al_2O_3 %	CaO %	F_2O_3 %	K_2O %	Na_2O %
Profile MZ-T1						
MZ-4B	78.38	12.84	0.38	2.24	1.91	0.75
MZ-4T	72.85	15.74	0.07	2.08	2.65	0.5
MZ-4M	71.77	16.6	0.12	1.63	2.46	0.13
MZ-05	75.23	13.11	0.26	1.75	1.52	1.4
MZ-06	65.34	14.99	0.1	2.07	2.83	0.09
MZ-07	65.73	17.17	0.1	2.54	1.65	0.02
Profile MZ-T2						
MZ-12A	68.44	15.53	0.77	1.46	0.33	4.31
MZ-12B	73.2	11.36	0.25	2.03	1.36	5.22
MZ-12C	75.17	10.9	0.15	2.57	1.93	1.23
MZ-12D	69.07	14.83	0.32	3.91	2.05	0.38

The samples from profile MZ-T2 showed a particularly restricted mineralogy composition when compared to profile MZ-T1 (Figure 3; Figure 4), presenting only a high concentration of albite and quartz (Figure 5). In addition, there was noticed a small concentration of magnesoferrite in sample MZ-07; however this may represent hematite, since both have similar peaks in the diffraction response.

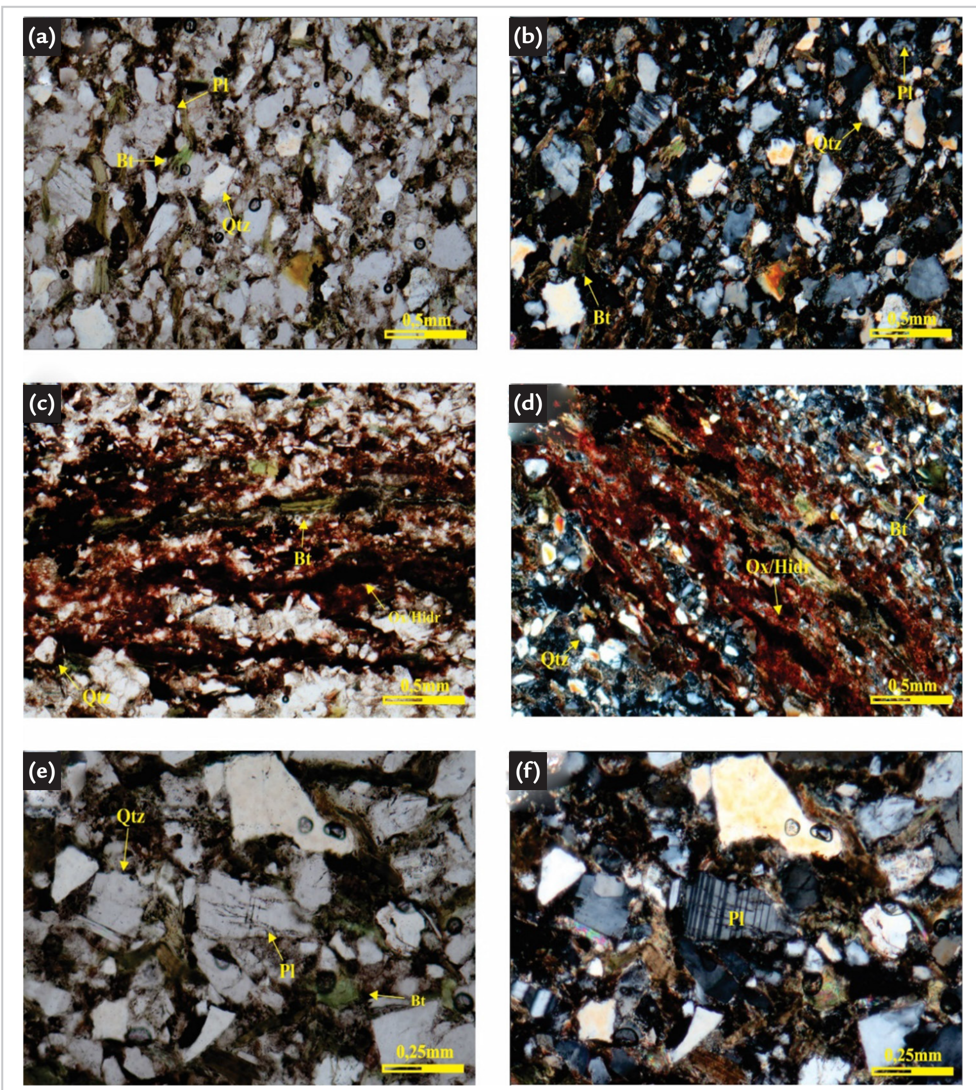

Figure 2 - Photomicrographs from profiles MZ-T1 and MZ-T2. a-b: crystals of quartz and plagioclase; c-d: iron oxide / hydroxide bands intercalated by filosilicate and quartz crystals; e-f: albite crystal with twinning second the Law of the Albite. Photomicrographs in transmitted and polarized light, respectively. Qtz: quartz; Pl: plagioclase; Bt: biotite; Ox / Hydr: iron oxide / hydroxide.

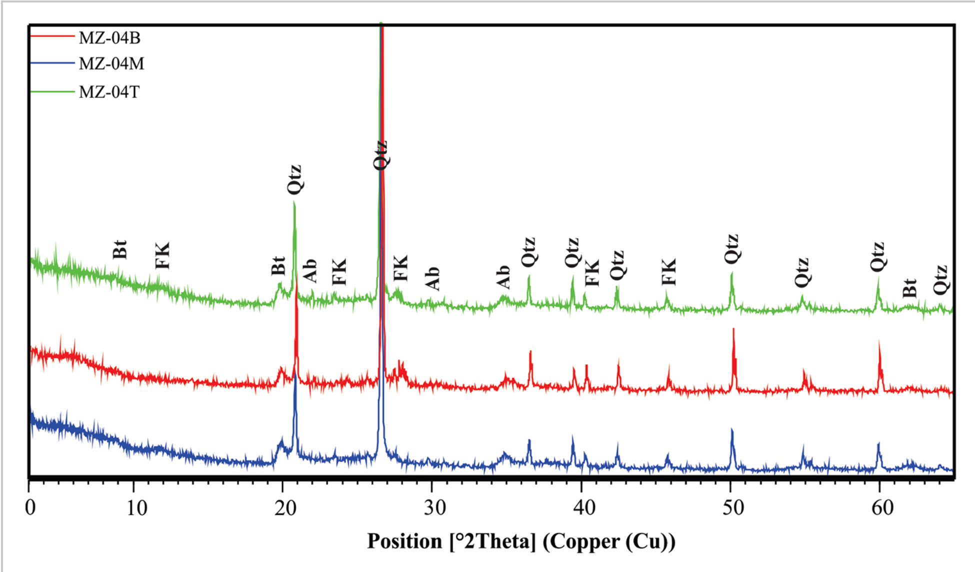

Figure 3 - Diffraction response of samples MZ-04B, MZ-04M and MZ-04T. Bt: biotite; Qtz: quartz; Ab: albite; FK: potassic feldspar.

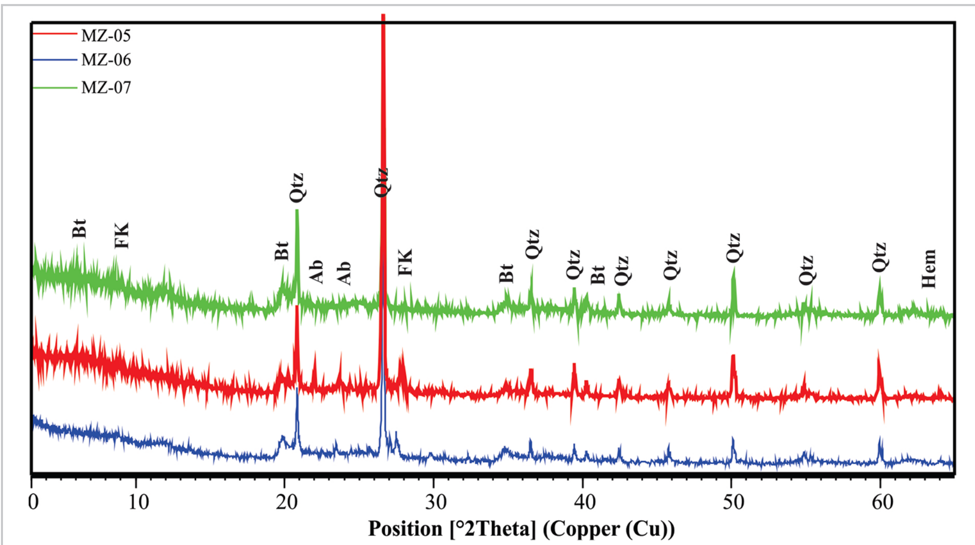

Figure 4 - Diffraction response of samples MZ-05, MZ-06 and MZ-07. Bt: biotite; Ab: albite; FK: potassic feldspar; Qtz: quartz; Hem: hematite.

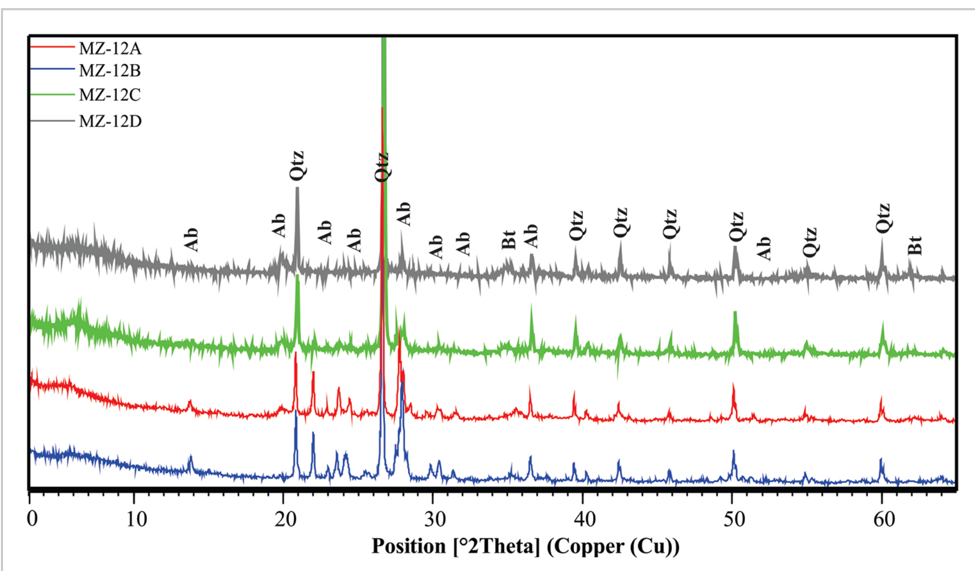

Figure 5 - Diffraction response of samples MZ-12A, MZ-12B, MZ-12C and MZ-12D. Ab: albite; Qtz: quartz.

3.2 Ceramic tests

The samples were separated pressed into rectangular specimens of 100 x 32 x 7 mm under a 10 MPa pressure and then separated for burning in a natural gas roll oven at sintering temperatures of 950 ° C, 1050 ° C and 1150 ° C for 24 hours. The mean values of linear retraction after burning (RLQ), instantaneous burst load (CRQ), flexural strength (MRFQ) and water absorption (AA) are set out in Table 2. Linear retraction values are shown with negative sign (-) to highlight the type of variation in the dimensions of the specimens. The sample MZ-04B was discarded due to problems during the burning process.

Table 2 - Parameters after burning.

Burning - 950⁰ C				
Sample	Linear retarction (%)	Breakpoint load (N)	Flexural strenght (N/mm²)	Water absortion (%)
Profile MZ-T1				
MZ - 4M	-4.61	171.76	12.41	6.88
MZ - 4T	-3.44	109.09	9.63	12.13
MZ - 05	-2.7	122.61	10.15	12.06
MZ - 06	-3.37	130.78	11.52	6.81
MZ - 07	-5.45	152.78	13.77	8.51
Profile MZ-T2				
MZ - 12A	-0.36	87.75	7	14.4
MZ - 12B	-1.53	114.13	9.78	8.71
MZ - 12C	-0.91	71.36	5.83	11.74
MZ - 12D	-1.31	66.78	5.93	11.34
Burning - 1050⁰ C				
Profile MZ-T1				
MZ - 4M	-9.86	187.94	18.79	2.64
MZ - 4T	-5.52	161.7	14.27	10.43
MZ - 05	1.76	141.67	11.13	12.89
MZ - 06	-5.37	153.98	13.77	5.14
MZ - 07	-10.61	174.83	16	6.83
Profile MZ-T2				
MZ - 12A	-3.91	157.78	13.55	8.21
MZ - 12B	-8.68	198.94	18.49	3.07
MZ - 12C	-1.69	118.26	9.22	12.49
MZ - 12D	-3.44	117.13	10.67	10.12
Burning - 1150⁰ C				
Profile MZ-T1				
MZ - 4M	-18.99	245.44	25.11	*
MZ - 4T	18.03	291.64	28	3.95
MZ - 05	-4.86	194.21	15.95	10.18
MZ - 06	-13.13	184.87	17.19	2.21
MZ - 07	-19.29	246.35	25.15	1.83
Profile MZ-T2				
MZ - 12A	-17.82	282.97	25.57	*
MZ - 12B	-15.56	274.45	26.52	*
MZ - 12C	-7.6	205.69	16.98	8.12
4.32MZ - 12D	-12.67	206.72	20.13	4.32

4. Discussion

The combination of petrography, X - ray diffraction, geochemical analysis and ceramic tests allowed the classification of Tatuí Formation lithotypes as a sequence of fine sandstones rich in silicon and aluminum oxides, composed of quartz, potassium feldspar/plagioclase (albite), and phyllosilicates. Some concentrations of iron oxides and zeolite were also observed in specific portions.

From the geochemical point of view, the material coming from the Tatuí Formation has a potential to be turned into ceramic masses. This is confirmed by the high concentration of silicon and aluminum oxides, which in the ratio SiO_2/Al_2O_3 indicates an appropriate concentration of refractory elements in the mass, where there was also observed a low content of calcium oxide (CaO), reflecting a low (or even non-existent) content of calcium carbonate ($CaCO_3$). In addition, the low concentration of iron oxide is also a favorable factor, since such concentration is reflected in little or no content of minerals rich in Fe, which can cause deformations generated by the excess of fusion and rapid transformations of the mineral phases.

The petrography and the diffractograms revealed a significant presence of albite and potassic feldspar in the samples. High concentrations of these minerals in ceramic masses can be a good indicator because these are directly related to the Na_2O and K_2O contents; oxides that act as good fluxing agents, favoring the sintering process.

Physically, the ceramic tests showed that the rates of linear retraction, instantaneous burst load and flexural strength gradually increase as the burning temperature increases, except for samples MZ-4T and MZ-05, which showed expansion during the burning procedure at 1150 º C and 1050 º C, respectively. This may be related to the quartz - α quartz - β reversion, since the β polymorph has a larger volume.

The water absorption rate was the parameter that showed the greatest heterogeneity in its values. In general, the samples presented a gradual decrease in the rate of absorption as the burning temperature increases. However, the samples MZ - 4M, MZ - 12A and MZ - 12B, due to the high degree of sintering generated after burning at 1150 º C, presented negative values of absorption, which indicates that the samples did not absorb water and even lost part of their weight due to the high rate of reduction of its porosity.

5. Conclussions

After the geochemical, mineralogical and physical tests, it was possible to classify the samples from the Tatuí Formation according to the norms ABNT NBR 13817: 1997 (ABNT, 1997b), taking the rate of water absorption as the main parameter of classification. For samples subjected to burning at 950 ° C, they were classified as coatings type BIIb (6 - 10%) and BIII (> 10%), the same classification can be applied to samples subjected to burning at 1050 ° C, except for samples MZ-4M and MZ-06, which can be classified as BIb and BIIa coatings, respectively (Table 3). At last, the samples subjected to burning at 1150 ° C were classified as BIa (MZ-4M), Bib (MZ-06, MZ-07), BIIa (MZ-4T, MZ-12D), BIIb (MZ-12C) and BIII (MZ-05). The samples MZ-12A and MZ-12B were discarded due to overburn (Table 4).

Table 3 - Possible uses for the material after burning at 950 °C and 1050°C.

Types of coating					
950⁰C / 1050⁰C					
Profile MZ-T1					
Sample	BIa	BIb	BIIa	BIIb	BIII
MZ - 4T		X			
MZ - 4M					X
MZ - 05					X
MZ - 06			X		
MZ - 07				X	
Profile MZ-T2					
MZ - 12A				X	
MZ - 12B				X	
MZ - 12C					X
MZ - 12D					X

Table 4 - Possible uses for the after burning at 1150°C. *: overburned samples

Types of coating					
1150^0C					
Profile MZ-T1					
Sample	BIa	BIb	BIIa	BIIb	BIII
MZ - 4T	X				
MZ - 4M			X		
MZ - 05					X
MZ - 06		X			
MZ - 07		X			
Profile MZ-T2					
MZ - 12A					*
MZ - 12B					*
MZ - 12C				X	
MZ - 12D			X		

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