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Spectroscopic characterization of recently excavated archaeological potsherds of Taquara/Itararé tradition from Tobias Wagner site (Santa Catarina – Brazil)

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ABSTRACT

Ceramic fragments provide one source of information for archaeologists about the way of life of different ancient population groups, especially concerning cultural identity, social organization and economics. By using scientific techniques of analysis, it is possible to elucidate the process of pottery production, as well as the specificities of the material used. In this paper, archaeological potsherd samples of the Taquara/Itararé Tradition collected in the research in Tobias Wagner site (TWG) were analyzed by spectroscopic methods and their micromorphology elucidated by electron microscopy. Semiquantitative elementary analysis using EDS showed that the elements in high content in the samples are Al, Si and Fe while in a lesser amount we found K and Ti. The sample TWG 219.8.2 presented accurate features of Zr, which may be a marker associated with the site where clay was collected. The main minerals that constitute the analyzed ceramics are kaolinite, quartz and haematite, and TiO_2 in the form of anatase present in the samples just in small quantities. The micromorphology of all samples is demonstrated to be very similar, presenting a heterogenic form with little particles of different geometries. With these results, it is estimated that the firing temperature of the fragments was at the most 850° C.

1. Introduction

Ceramic vestiges found in archaeological sites are frequently considered as materials that identify the horticulture and/or the agriculture practice by ancient population. In the course of the process of ceramic manufacture, the artisans have to make choices, concerning the clay used, antiplastic agent additional to paste, potsherds manufacture techniques, firing, decoration, etc., which are carried out considering as well as the cultural aspects as performance characteristics. This set of choices specifies the operative chain of ceramics production and it can offer important information for the knowledge of ceramics cultural repertory, allowing a better comprehension of its production technology and its changes during time (Van Der Leeuw, 1993; Orton et al., 1993).

Through the ceramic vestiges analysis, it is possible to obtain information about the technology used on its production and application by a specific cultural group. For a better comprehension about this particular productive process it is necessary to conciliate both the result from archaeologic analysis focused on technologic characteristics of production, including technique features related to raw materials, related to processing forms, to the choices of performance, construction and use of ceramics vestiges – including vestiges' morphologic and formal aspects, as well as the physicochemical analysis.

Therein, with the aim to a better comprehension of the manufacture process and structural characteristics of the ceramics vestiges from Taquara/Itararé[1] Tradition collected in Tobias Wagner[2] archaeological

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[1] Taquara/Itararé Tradition ceramic is associated to preterit occupation developed by groups speaking the Jê family language. In the south of Brazil, in general, these groups consist on the ancestral from indigenous groups Kaingáng and Xokleng. Nowadays, these population live in indigenous lands nestled in the plateau and mountains in the states of São Paulo, Paraná, Santa Catarina and Rio Grande do Sul.

[2] The group from Laboratório de Estudos Interdisciplinares em Arqueologia (LEIA) from Universidade Federal de Santa Catarina (UFSC), coordinated by professor Dr. Lucas Bueno, had three excavation stages in Tobias Wagner archaeological site between 2014 and 2015. Three pit houses and a feature on surface (denominated Area 1) had interventions, totalizing 10,25m^2 of area excavated from superficial plane. Through the excavation, eight stratum which form the site were identified. In seven of them they were collected archaeological vestiges. In general, the material found consist on archaeobotanical vestiges (charcoal, seeds and pinewoods node), lithic (chipped, polished and pecked ones) and ceramic fragments associated to Taquara/Itararé Tradition. One charcoal sample collected on Area 1 was dated in 300 ± 30 A. P (Beta-410430).

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site, nestled in the south of Brazil, they were employed as part of this research spectroscopic analysis as FTIR, μ-Raman and EDS, as well as scanning electron microscopy for the morphologic study. It is important to say that it is a set of techniques widely adopted to characterize these artifacts and the correlation with its respective manufacture (Manoharan et al., 2015; Manoharan et al., 2007; De Benedetto et al., 2002; Shillito et al., 2009); then, it is possible to emphasize that studies of this type are widely complex and only the use of different analytic techniques can provide a suitable result (Silvano et al., 2003).

2. Materials and methods

2.1. Excavation and sample's collection

Tobias Wagner archaeological site (TWG), nestled in Lomba Alta, countryside of Alfredo Wagner, state of Santa Catarina, Brazil, under coordinates UTM 22J 658458/6932788 (WGS84), is formed by 18 pit houses (Fig. 1). It presents yet features and occurrences on surface. The vestiges are dispersing on an area of approximately 2000 m^2. Part of the site is covered by Atlantic Forest, and on the rest there is *pinuselliottii* plantation. The ceramic vestiges were found too fragmented and they were collected in profundity of 1,30 m in the archaeological record of a pit house (E01). All samples are come from strata 02 and 03, which consist on the base of the pit house (E01) – context of ancient occupation of this space. These vestiges were collected, packed individually, tagged and carried to laboratorial analysis. It can be observed on Fig. 2 a photograph of each of the fragments collected and analyzed.

2.2. Fourier transform infrared spectroscopy – FTIR

The infrared spectra were collected in the equipment JASCO, an spectrometer model FTIR-4100 with 4 cm^{-1}resolution, in pastilles of KBr in which approximately 5 mg of each sample was homogenized for analysis, and they were performed in the minimum three different places in each sample to confirm the results, and all the spectrum were collected with 64 scans.

Fig. 2. Ceramic samples collected in Tobias Wagner site – TWG.

2.3. Micro Raman spectroscopy - μ-Raman

Samples were spread on a mirror glass plate and analyzed with a Bruker Senterra micro-Raman spectrometer. The best spectra were collected using 532 nm wavelength line with 10 mW of illumination power. The exposure time was 10.0 s and 5 coadditions were taken. The macro configuration generated very bad spectra, so an aperture of 50 μm was used to get real confocal measurements of isolated grains. The scattered beam was collected by an Olympus 50× objective.

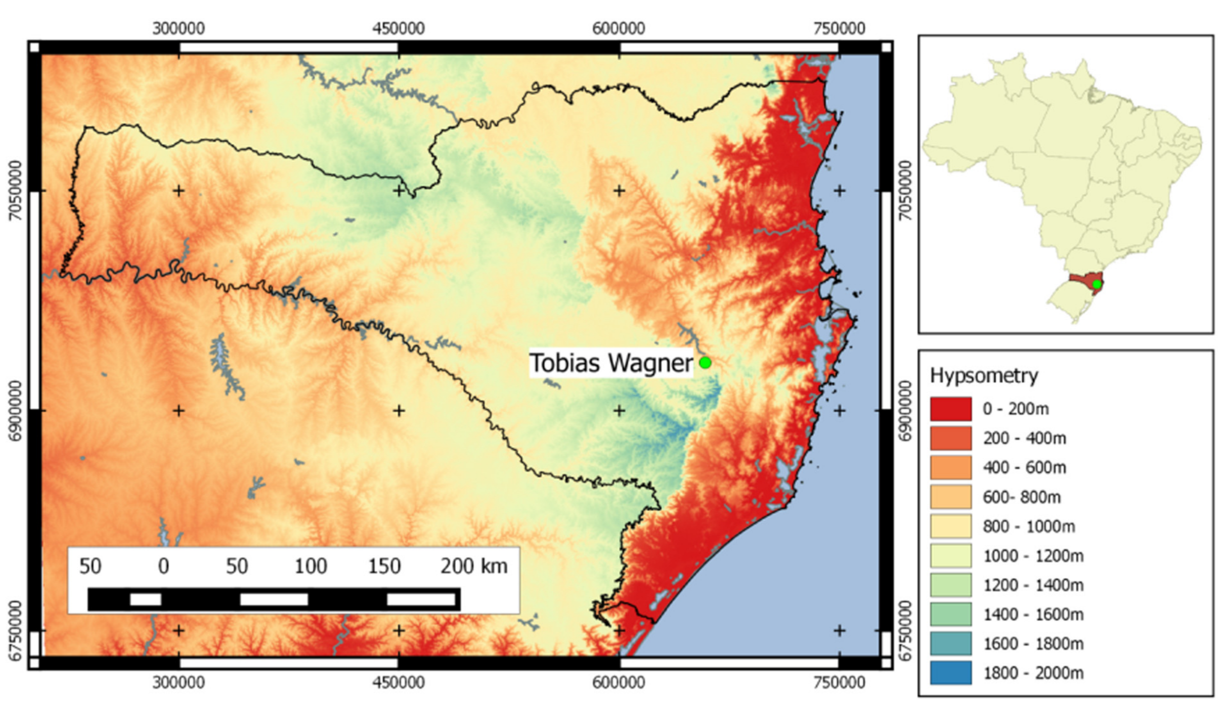

Fig. 1. Map with Tobias Wagner archaeological site location in the state of Santa Catarina and in Brazil.

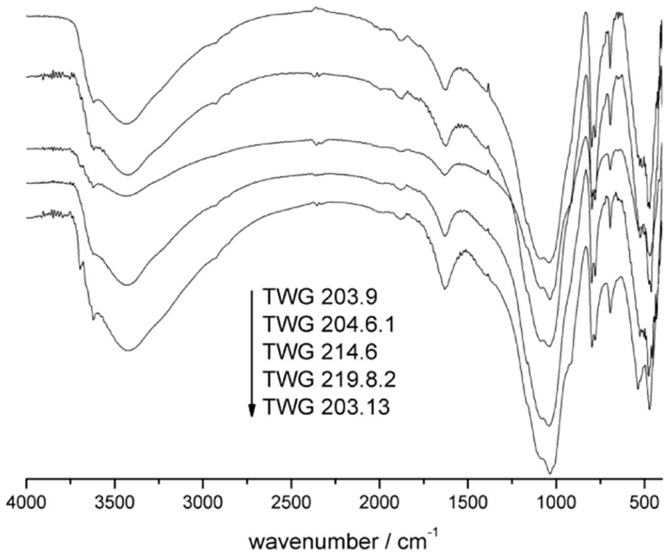

Fig. 3. FTIR spectra of each potsherd samples.

2.4. Scanning electron microscopy with X-ray microanalysis – SEM-EDS

The morphologies of each fragment were obtained by micrography using a scanning electron microscope model Phenom Prox-X with increase of 3100-3600×. The of EDS spectra were collected in a spectrometer by dispersive energy of X-rays connected to the scanning electron microscope using a 15 kV accelerating voltage. They were realized also elementary mappings with the following parameters: Map resolution of 64 scans and 50 ms pixel time.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy – FTIR

The infrared spectra of the collected samples from potsherds fragments can be observed on Fig. 3. All the samples present similar spectrum, which can be observed the bands between 3621 and 3626 cm^{-1} attributed to ʋO—H stretching of hydroxyl groups in a crystalline system (Kiruba and Ganesan, 2015), 3416–3425 cm^{-1} e 1624–1633 cm^{-1} related to ʋO—H possible water molecules absorbed (Velraj et al., 2012) in mineral structure, 1034–1040 cm^{-1} related to ʋSi—O stretching presents in clay minerals (Russell, 1987), bands between 777 and 779 cm^{-1} and 693–695 cm^{-1} are attributed to ʋSi—O—Si bending in quartz (Palanivel and Velraj, 2007). In addition, the ʋFe—O stretching can be attributed to the bands between 528 and 537 cm^{-1} and 469–471 cm^{-1} characterizing the iron oxide in form of Haematite (Legodi and de Waal, 2007), which is also observed in the μ-Raman spectra. The samples TWG 203.9, TWG 204.6.1, and TWG 219.8.2 presented bands between 2848 and 2922 cm^{-1} attributed to ʋC—H stretching, indicating vestiges of organic material in the fragments. The Table 1 presents a summary of the found bands and the respective attempt of characterization.

On the infrared spectrum, the samples TWG 204.6.1, TWG 214.6, and TWG 203.13 present two bands in the region which corresponds to hydroxyl groups in crystalline system, this evidence can be associated to the possibility of presence of the kaolinite mineral, $Al_2Si_2O_5(OH)_4$, and this proposition is in compliance with results from EDS in which can be observed Al presence in the samples. In addition, bands between 3624 and 3621 cm^{-1} can be attributed to the hydroxyl group in tetrahedral environments and the band in 3693 cm^{-1} attributed to symmetric in-phase stretching in accordance with the characterization of this kind of material in the literature (Madejová, 2003; Farmer, 2000). It is also observed the absence of bands in 915 cm^{-1}, which is a characteristic band of ʋAl—OH in octahedral systems, revealing that all samples were manufactured in temperatures higher than 500 °C (Raja Annamalai et al., 2014; Elsass and Oliver, 1978).

For these samples, the absence of bands related to carbonaceous materials was corroborated by the negative test for carbonate by means of reaction with hydrochloric acid, which confirmed the absence of carbonate-based minerals.

3.2. Micro Raman spectroscopy - μ-Raman

The typical micro-Raman spectra obtained for the TWG samples are shown in Fig. 4. It is observed characteristic bands in 398, 515, 636 cm^{-1} attributed to TiO_2 as polymorphic anatase (Frank et al., 2012), identified in particles heterogeneously distributed as little crystals, it has been verified in other archaeological ceramics (Costa et al., 2004). The presence of this mineral reveals a firing temperature at most 850 °C was used in the manufacture of ceramics because anatase converts itself rapidly to rutile form in temperatures higher than this (Smith and Clark, 2004). Characteristic bands in 206, 263, 354, 393, 462 and 800 cm^{-1} are attributed to quartz (Genestar and Pons, 2005) which corroborated the results obtained by FTIR.

The characterization of iron oxide in this kind of sample is not so common (Froment et al., 2008). So, in our case, a double band in 226 and 286 cm^{-1}, and a broad band in 1320 cm^{-1}, can be associated to presence of haematite (Cavalheria et al., 2010) (α-Fe_2O_3), since it has been characterized also by FTIR.

3.3. Scanning electron microscopy with X-ray microanalysis – SEM-EDS

The SEM-EDS technique is one of the most versatile in terms of applicability in morphological characterization of archaeological ceramic artifacts, as well as the semiquantitative analysis by EDS (Frahm, 2014). The collected micrographies of all samples are presented on Fig. 5. The samples morphologies from the TWG series are very similar and present a heterogeneous form, containing irregular little particles from different geometries and sizes. This microstructure is characteristic for ceramics manufactured in a single-step manufactured with moderated temperatures (Colomban et al., 2004; Krapukaityte et al., 2006).

The potsherds elementary composition can be observed through the EDS spectra, Fig. 6, the semiquantitative analysis are presented in Table 2, and the elemental mapping are found in Fig. 7. First of all, it can be attribute the nature of clay minerals as calcareous or non-calcareous, identified by CaO percentage (Maniatis and Tite, 1981), in which higher than 6% they are known as calcareous clays, and lower than 6% as non-

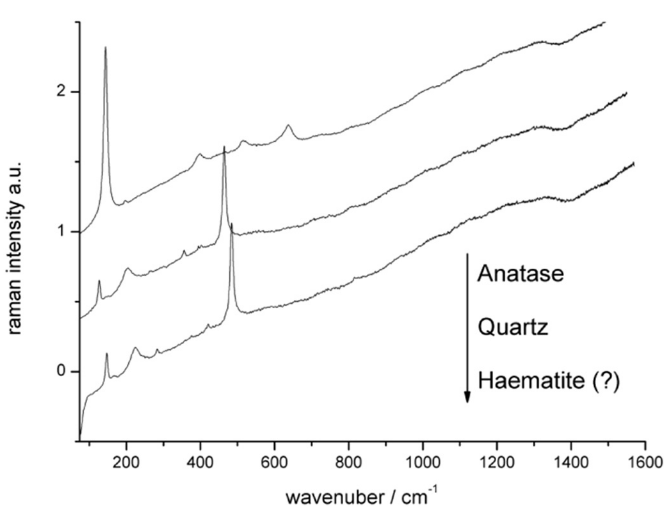

Fig. 4. Typical Raman spectrum observed in the TWG samples.

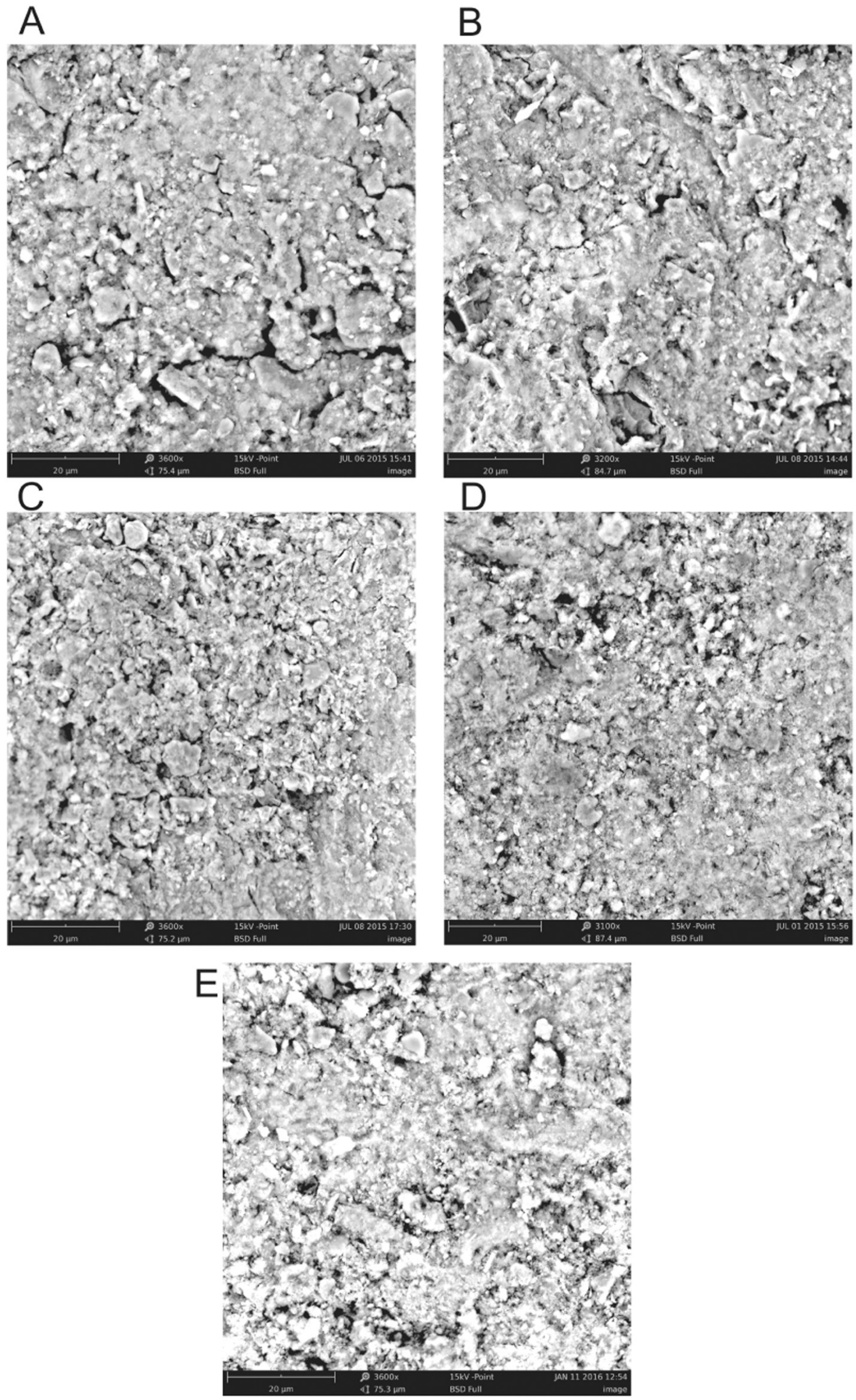

Fig. 5. Micrographies from potsherds samples: (A) WG 203.9, (B) TWG 204.6.1, (C) TWG 214.6; (D) TWG 219.8.2, (E) TWG 203.13.

calcareous. The samples from TWG series are characterized by calcium absence, which characterize them in relation to the clay minerals nature as non-calcareous clays, not even in the form of calcium carbonate as it was affirmed previously by FTIR. The absence of calcium and consequently aluminosilicate calcium can indicate a superior limit firing temperature of 850 °C (Ravisankar et al., 2013), converging to data achieved by μ-Raman in which TiO_2 form corresponds to this temperature.

The elements Al, Si and Fe showed up as the one in major content in all samples, mainly because of the presence of alumina, quartz and iron oxide respectively, as well as some content of kaolinite, all of them observed by FTIR and μ-Raman.

In relation to minority elements, it is notable to mention potassium. It is present in all samples in quantities up to 2%. Potassium-based compounds are common fluxing agents in the production of ceramic materials, promoting initial sintering and the extensive vitrification (Mitri et al., 1999). Taking this feature in account, the presence of K in the samples can be associated to little quantities of potassium feldspar, but it requires a new and deeper investigation.

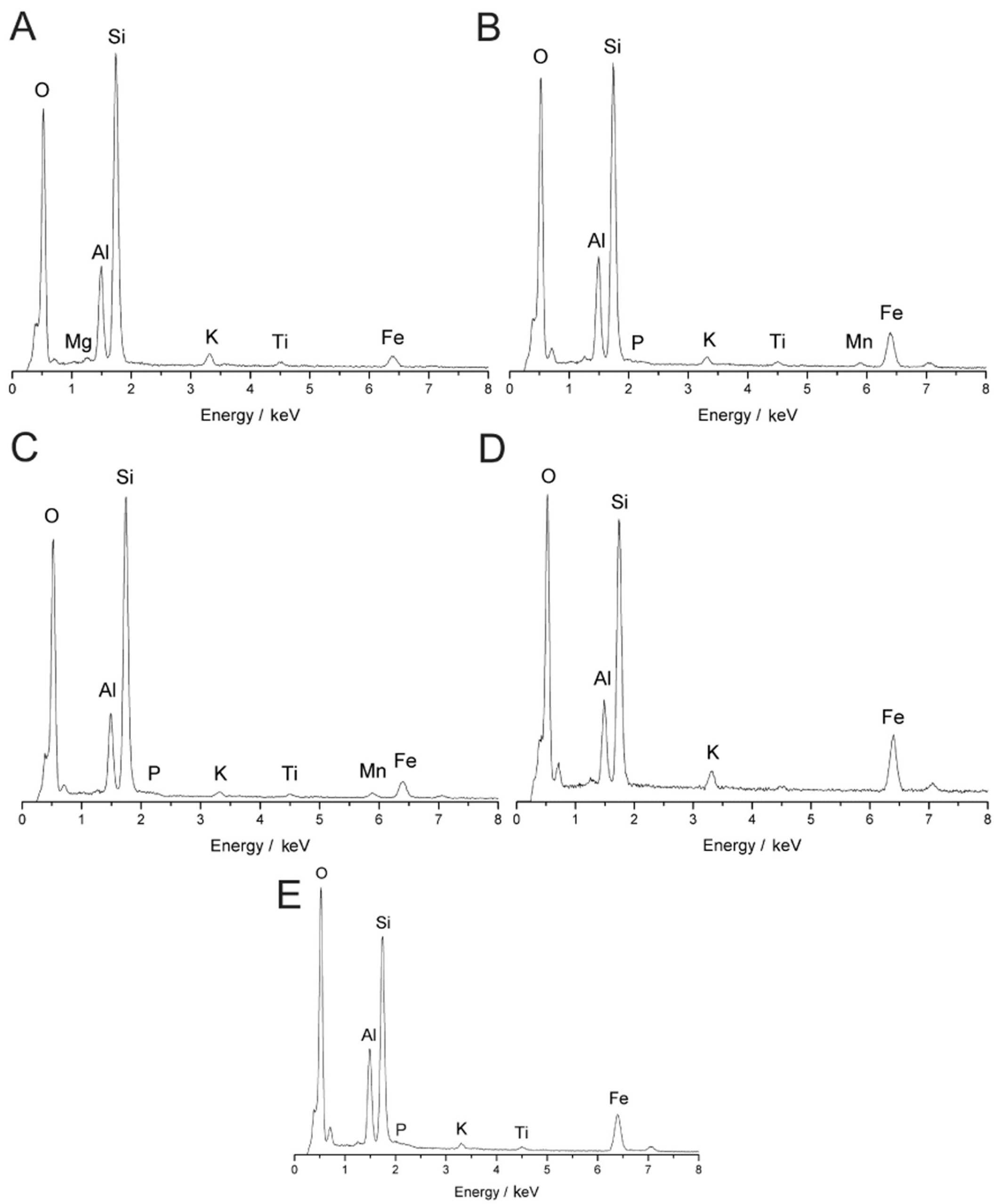

Fig. 6. EDS spectra of (A) TWG 203.9, (B) TWG 204.6.1, (C) TWG 214.6; (D) TWG 219.8.2, (E) TWG 203.13.

Another expressive element present in little quantity is titanium, of which only traces were found in sample TWG 219.8.2. Many authors mention titanium as well potassium presence in archaeological ceramics material, in the form of oxides (Velraj et al., 2012; Smith and Clark, 2004; Genestar and Pons, 2005; Froment et al., 2008; Cavalheria et al., 2010; Frahm, 2014; Colomban et al., 2004; Krapukaityte et al., 2006; Maniatis and Tite, 1981; Ravisankar et al., 2013; Mitri et al., 1999; Weiss et al., 2015); since both oxides act as fluxes in clays. The presence of Ti in both samples confirms the result obtained by μ-Raman that characterized the TiO_2 anatase form in the samples.

The magnesium element could only be quantified in sample TWG 203.9 and its indications were detected in sample TWG 203.13. Magnesium oxides are also characterized as fluxes (Ravisankar et al., 2013), and Mn was quantified in samples TWG 204.6.1 and TWG 214.6, considering that in the sample TWG 219.8.2 there were identified only indications, manganese can be associated to clay minerals forming microcrystalline aggregations, and in oxide forms (Chukhrov et al., 1980).

Another interesting point was the detection of little punctual granules of Zr in sample TWG 219.8.2, Fig. 8, and the combined presence of silicon indicate a possible zirconium silicate (Chukhrov et al., 1980) or even a marker, which means that zirconium's presence in clay minerals in this context can be associated to marine sediment. Regarding this, it is possible that the clay used to produce the pottery was extracted from marine sediments, or even a mixture of clays extracted from different places (Goldschmidt, 1954; Goffer, 2008).

The morphological and elementary similarities present in all the samples from TWG series present that probably all the material found were produced in the same area of manufacture, and probably using the same technique.

4. Conclusions

FTIR spectroscopy, μ-Raman and SEM-EDS techniques, were used on characterization and morphologic study of five archaeological ceramic

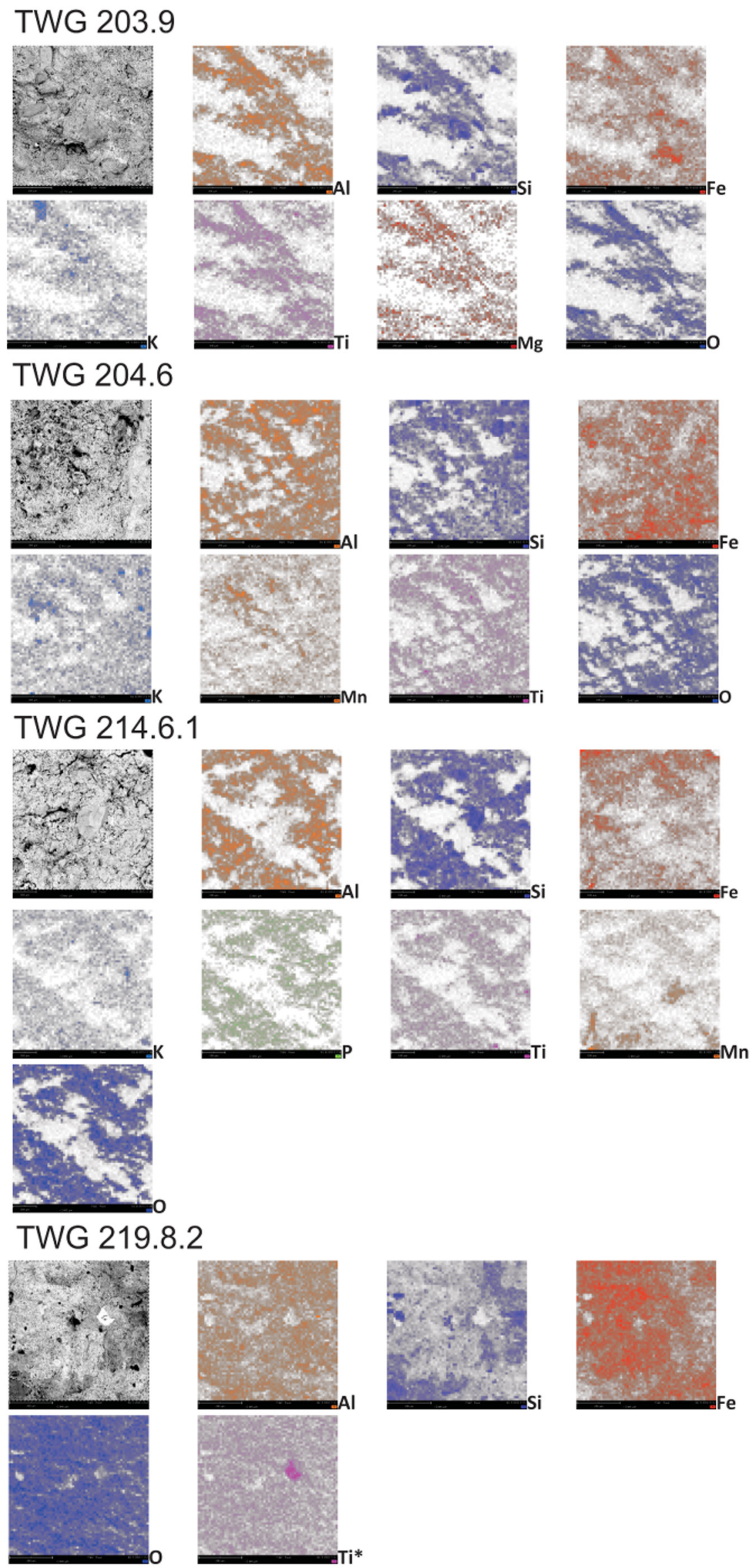

Fig. 7. Element maps of TWG potsherd series.

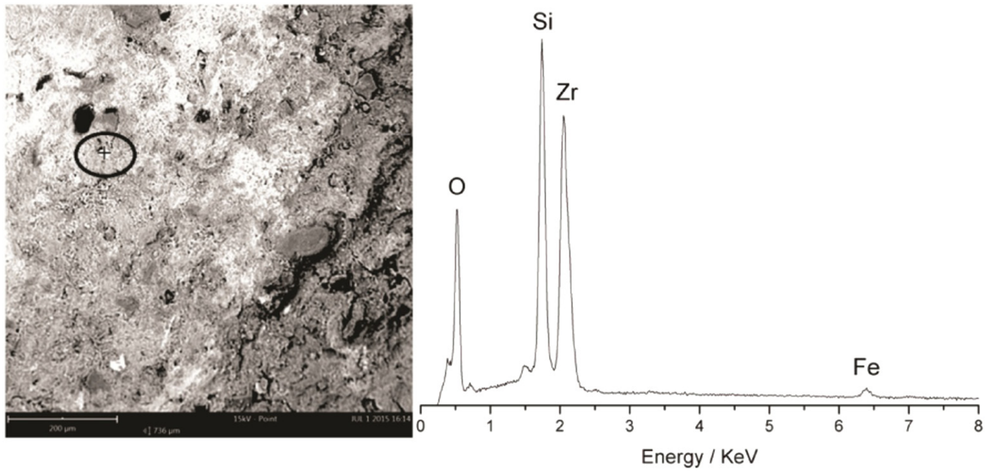

Fig. 8. Micrography showing in detail the area in which zirconium was found in the sample TWG 219.8.2 and its corresponding EDS spectrum.

Table 1
Overview of infrared absorption frequencies (cm^{-1}) found in each sample, as well as the attempt of assignment.

TWG 203.9	TWG 204.6.1	TWG 214.6	TWG 219.8.2	TWG 203.13	Assignment
3626 w	3624 w, 3693 w	3624 w, 3693 w	3624 w	3621 w, 3693 w	O—H (crystalline hydroxyl)
3425 m	3422 m	3426 m	3422 m	3416 m	O—H (adsorbed water
2922 w	2920 w, 2848 w	–	2918 w, 2853 w	–	C—H (organic)
1633 m	1624 m	1629 w	1624 m	1627 m	O—H (adsorbed water)
1040 s	1033 s	1036 s	1042 s	1034 s	Si-O (clay minerals)
778 m	779 m	777 m	779 m	778 m	Si—O (quartz)
695 m	693 m	693 m	694 m	694 m	Si—O (quartz)
537 w	530 m	528 w	526 w	535 m	Fe—O Fe_2O_3 (Haematite)
469 m	470 m	473 m	477 m	471 m	Fe—O Fe_2O_3 (Haematite)

s – strong, m – medium, w – weak.

samples from Taquara/Itararé Tradition, collected in Tobias Wagner site, and they are related to Jê meridional human groups. The FTIR analysis enlightened the presence of quartz, haematite and the kaolinite in all the samples. Besides that, the samples TWG 203.9, 204.6.1 and 219.8.2 presented characteristic bands attributed to ιC—H stretching, indicating organic material vestiges in these fragments. The μ-Raman results confirmed the presence of haematite and quartz's in all the fragments, and elucidated TiO_2 in anatase form. The characterization by EDS made clear that the elements in higher content in all samples are Al, Si and Fe, which is in agreement with the FTIR and μ-Raman results. All samples presented K and Ti as minority elements and the samples TWG 203.9 and 203.13 presented indications of Mn. In addition, the sample TWG 203.13 presented zirconium traces which can be linked to clay collected from marine sediments. No sample presented calcium in EDS analysis, and clays were classified as non-calcareous. With these results, it is estimated that the artifact firing temperature was at the most 850 °C. These results helped to comprehend a little bit more about the cultural aspects from Jê meridional group that inhabited Tobias Wagner site in the past, settled in the mountains of Santa Catarina state, as well to elucidate historical facts, the preservation of archaeological and cultural patrimony and they also illustrated how interdisciplinary studies can contribute to make possible a better and refined comprehension of the past.

Table 2
Elemental analysis (% weight) found in each potsherd sample.

Sample	Al	Si	Fe	K	P	Ti	Mg	Mn	O
TWG 203.9	6.6	20.3	15.4	1.3	[a]	0.8	0.3	–	55.2
TWG 204.6.1	7.0	19.5	13.3	0.9	0.7	0.7	–	1.0	56.8
TWG 214.6	6.9	22.0	7.1	0.7	0.7	0.7	–	1.6	60.3
TWG 219.8.2[b]	6.3	17.5	18.8	2.0	–	[a]	–	[a]	55.4
TWG 203.13[c]	8.4	18.3	9.7	0.5	1.1	0.5	[a]	–	61.4

[a] Punctual traces of the elements.
[b] Punctualtrace of zirconium.
[c] Punctual traces of sodium and chloride – the punctual traces was only observed in point and shoot EDS mode.

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