Oxidation states of iron as an indicator of the techniques used to burn clays and handcraft archaeological Tupiguarani ceramics by ancient human groups in Minas Gerais, Brazil

D. L. Floresta · J. D. Ardisson · M. Fagundes · J. D. Fabris · W. A. A. Macedo

Abstract Ceramics of the Tupiguarani Tradition typically have in common the burning characteristics, their forms and decoration motifs. Dating such ceramic pieces with the radiocarbon method indicate that these artifacts were probably handcrafted between 1,500 and 500 years before the present. Fragments ceramic utensils were collected in the archaeological site of Beltrão, in the municipality of Corinto, state of Minas Gerais, Brazil. A fragment of about 50 mm in diameter and 15 mm thick, with a color gradation across the ceramic wall ranging from red, on one side, grayish, in the middle, and orange, on the opposite side, was selected for a more detailed examination. The fragment was transversely cut and a series of subsamples were separated from different points along the piece wall, in layer segments of ∼3 mm. All subsamples were analyzed with Mössbauer spectroscopy at room temperature and 80 K. Results reveal that hematite is the magnetically ordered phase. A Fe^{2+} component (relative spectral area, 50 %) appears for the grayish subsample. According to these first results, the red subsample seems to be the side that had direct contact with fire used to burn the precursor clay in air. The grayish middle layer is probably due to the clay mixed with some ashes. Mössbauer data reveal that the orange layer, corresponding to the opposite side of the ceramic relatively to the direct fire, does contain about the same $Fe^{2+}:Fe^{3+}$ ratio but much lower proportion of $\alpha\text{-}Fe_2O_3$ than the red layer.

Keywords Tupiguarani ceramics · Archaeometry · Iron oxides

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1 Introduction

Ceramics of the Tupiguarani Tradition are found in many parts throughout the Brazilian territory. They typically have many similarities mainly concerning the primitive technique of burning conditions, their forms and decoration motifs. Data on selected pieces obtained with the radiocarbon method indicate that these artifacts are dated from between 1,500 and 500 years before the present [1, 2]. Fragments of a Tupiguarani pottery found in the archaeological site known as Beltrão (location map, Fig. 1), in the municipality of Corinto, state of Minas Gerais, were identified and collected by researchers of the Laboratory of Archaeology and Landscape Studies of the Federal University of Jequitinhonha and Mucuri Valleys, in Diamantina, also in Minas Gerais. A selected fragment of about 15 mm thick, with a color gradation across the ceramic wall ranging from red, on one side, grayish in the middle and orange on the opposite side, was chosen for a more detailed examination.

2 Methods

The sample collected from the Beltrão archaeological site was first transversely cut so that a quarter of the ceramic piece (Fig. 2) was removed for further image analyses. The segmented quarter was divided into three subsamples of 5.0 mm thick each according to their colors from the (i) orange; (ii) grayish and (iii) red layers. These three subsamples were metalized, by coating them with a palladium-gold alloy, and imaged in a Jeol scanning electron microscope (SEM), Model JSM-5310. The remaining part of the ceramic sample was also sampled in a series of subsamples from different depths across the wall, in layer segments of $\sim$3 mm, from the orange side up to the opposite red side of the ceramic wall. The subsamples were ground and labeled according to the depth across the fragment wall: 0 mm (orange side), 3 mm, 6 mm, 9 mm, 12 mm and 15 mm (red side). The subsample 9 mm was actually obtained from the grayish middle layer. These powdered subsamples were analyzed with X-ray fluorescence (XRF) and diffraction spectroscopy (XRD) and ^{57}Fe Mössbauer spectroscopy at room temperature ($\sim$298 K) and at 80 K.

The X-ray fluorescence analysis was made with an energy dispersive X-ray fluorescence spectrometer, Shimadzu EDX-720, with rhodium tube and silicon-lithium detector. Each of these subsamples was put in a sample holder with a diameter of 5 mm; data were collected with sample under vacuum.

The powder X-ray diffraction data were collected in a Rigaku diffractometer equipment, model D\MAX ULTIMA, with $\theta - \theta$ goniometer and copper X-ray tube ($\lambda_{K\alpha} = 1,5418740$ Å), within a scanning range of 4° to 80° 2θ; the velocity of the goniometer was set to 4° 2θ/min, with a current of 30 mA and tension of 40 kV.

^{57}Fe-Mössbauer spectra were obtained with a conventional transmission geometry setup, using constant acceleration regime, with a $\sim$50 mCi ^{57}Co/Rh gamma-ray source kept at room temperature. Measurements were made at room temperature (RT) and 80 K. Isomer shift values were quoted relatively to the metallic αFe. Resonant curves were fitted to Lorentzian functions through least-square fitting
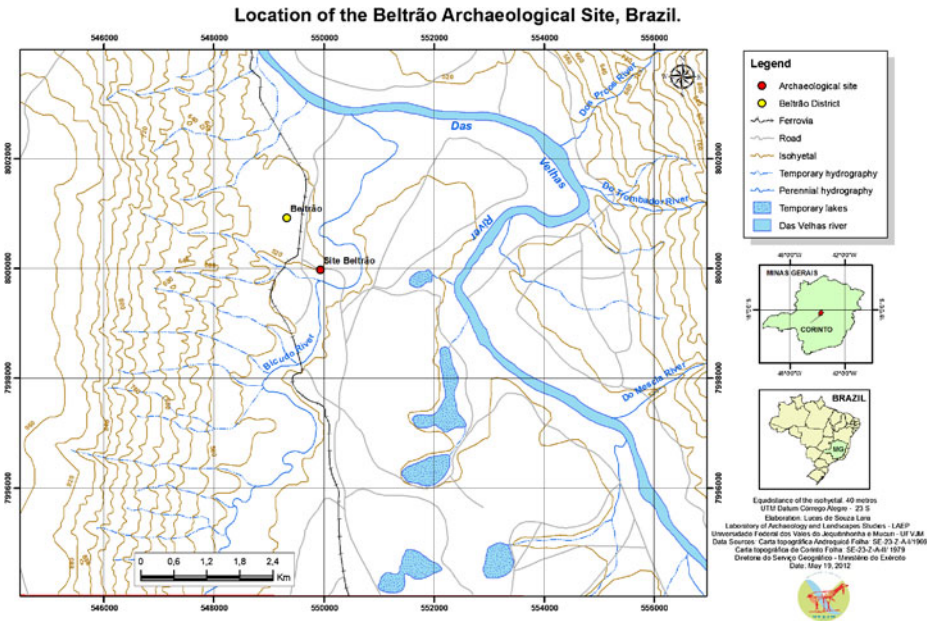
Fig. 1 Geographical location of the archaeological site of Beltrão, in Corinto, state of Minas Gerais, Brazil

Fig. 2 The ceramic fragment from the Beltrão archaeological site, with the *red* upper, the *orange* bottom and the *grayish* middle layers along the transverse cut. Colors are thought to reflect different oxidation conditions according to the local chemical environment during clay burning. Subsamples were separated from different depths all along the cut ceramic wall. The indicated scale is in cm

with software NORMOS™-90 (developed by R. A. Brand, at Laboratorium für Angewandte Physik, Universität Duisburg, D-47048, Duisburg-Germany).

3 Results and discussion

SEM images (Fig. 3) indicate that the material is uniformly similar for all depths. It was not possible to measure grain sizes as these ceramic materials consist of very finely divided and firmly compacted particles.

According to the X-ray fluorescence results, the elementary composition does not clearly vary with the depth in the sample. For the probed chemical elements Si, Al,

Fig. 3 Scanning electron microscope images for the three subsamples, according to their colors, obtained from the Tupiguarani ceramic sample of the archaeological Beltrão site: **a** *orange*, **b** *grayish* and *red* **c** layers
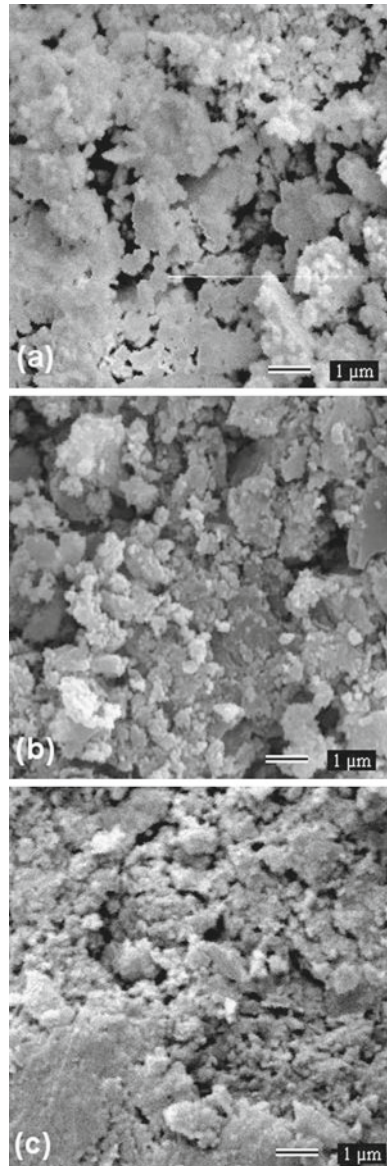
Fe, Cl and K there were found contents between 1 and 25 mass%. Contents for Ti, Mg, Ba, Ca and S were found to be less than 1 mass%. For all other elements contents were less than 0.1 mass% (Fig. 4).

The powder X-ray pattern obtained for each subsamples reveals essentially the same reflection peaks (Fig. 5); the pattern for the red subsample shows better resolution. An independent pattern was collected for the red subsample, with velocity of the goniometer corresponding to 0.16° 2θ/min. This pattern (Fig. 6) was used to better identify the main occurring minerals, by comparing it with the COD
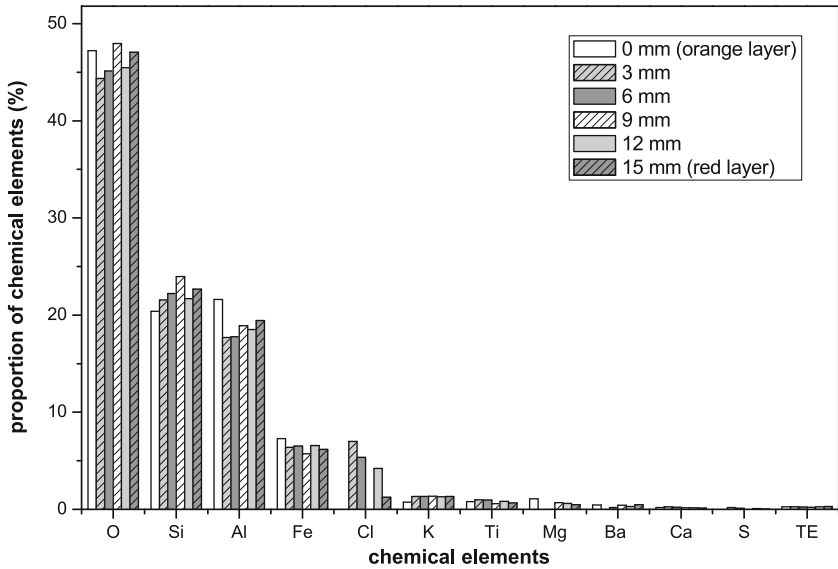
Fig. 4 Chemical composition data as determined with X-ray fluorescence spectroscopy. The labeled subsamples were collected from different depths all along the transected wall from the Tupiguarani ceramic sample of the archaeological Beltrão site. TE (meaning trace elements) = contents corresponding to less than 0.1 mass% (P, Pb, Cr, Mn, Ni, Zr, Sc, Ac, Ir, Rb, Zn, Y and Sr)

Fig. 5 Powder X-ray diffraction patterns for the subsamples of Tupigurani ceramic from the archaeological Beltrão site, collected along the transected section at different depths across the wall of the ceramic fragment
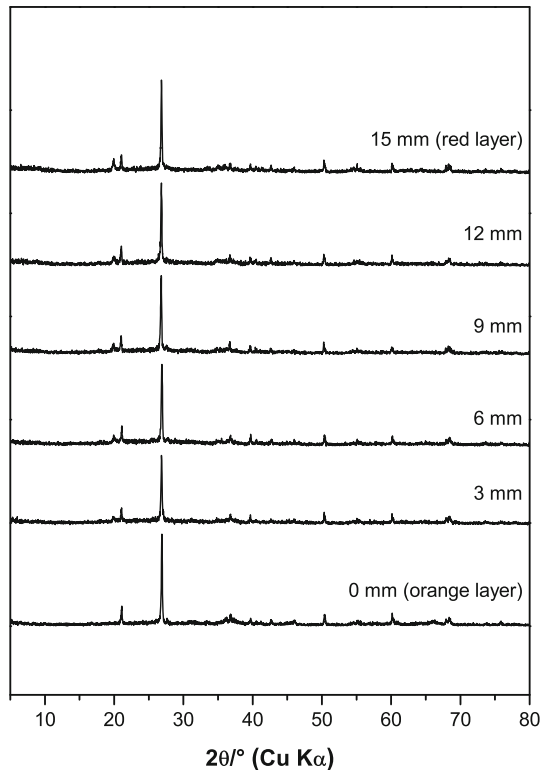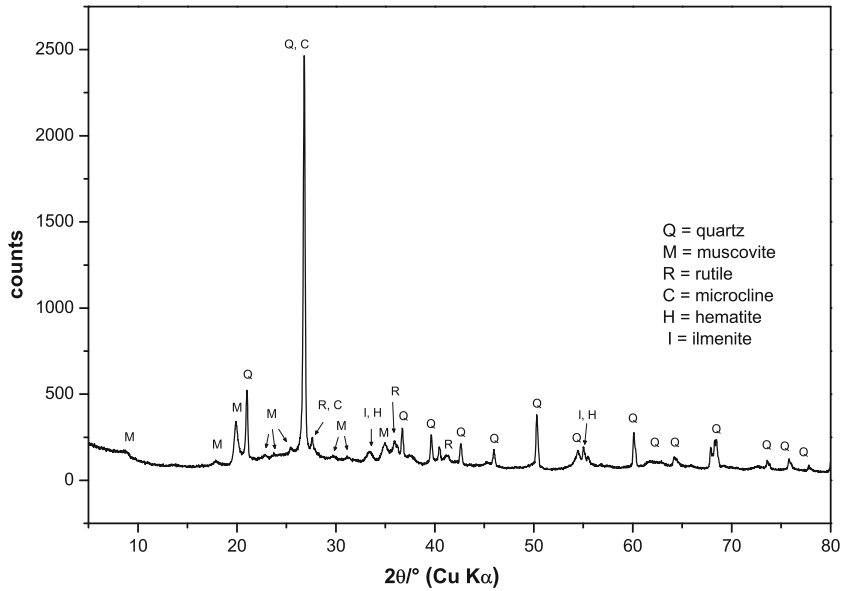
Fig. 6 Powder X-ray pattern for the subsample corresponding to the *red* layer collected from the transected wall of the Tupiguarani ceramic sample of the archaeological Beltrão site

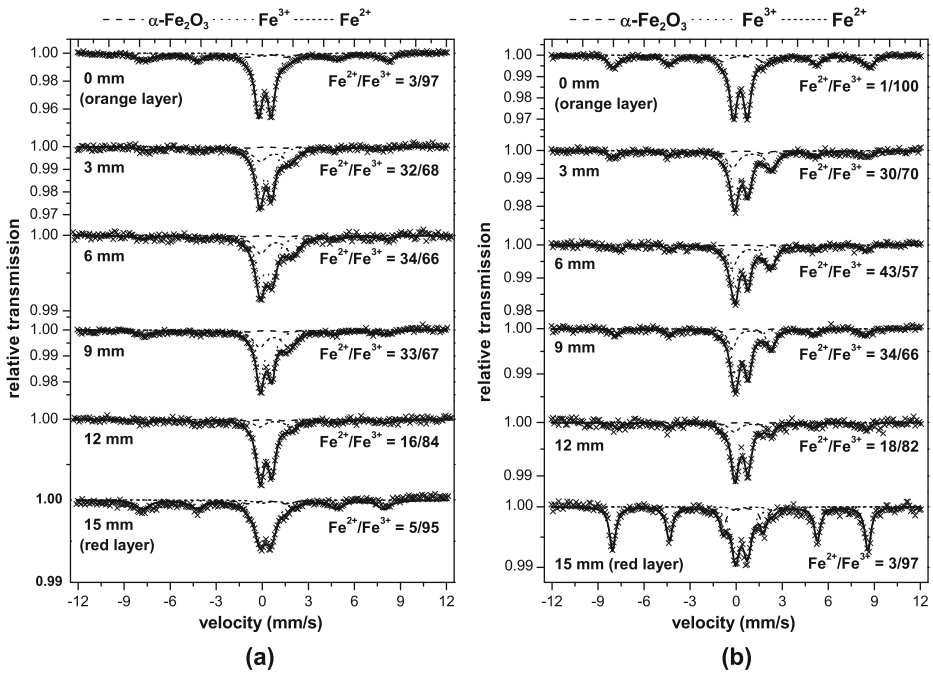**Fig. 7** ^{57}Fe-Mossbauer spectra for subsamples of materials collected from different depths across the wall of the Tupiguarani ceramic sample from the archaeological Beltrão site. Data were collected with samples at **a** room temperature (∼298 K) and **b** 80 K

Table 1 ~298 K ^{57}Fe-Mössbauer parameters for subsamples from different depths along the transected wall of the Tupiguarani ceramic sample of the archaeological Beltrão site

Subsample	Site	δ ($\pm0,0$ 5) mm/s	Δ, ε (±0.05) mm/s	B_{hf} ($\pm$ 0,5) tesla	RA (±1) %
0 mm (orange layer)	α-Fe$_2$O$_3$	0.35	−0.14	49.1	37
	Fe^{3+}	0.27	0.83		60
	Fe^{2+}	0.98	1.80		3
3 mm	α-Fe$_2$O$_3$	0.32	−0.13	48.6	18
	Fe^{3+}	0.31	0.83		50
	Fe^{2+}	0.90	1.92		32
6 mm	α-Fe$_2$O$_3$	0.31	−0.16	48.8	15
	Fe^{3+}	0.34	0.78		51
	Fe^{2+}	1.01	1.99		35
9 mm	α-Fe$_2$O$_3$	0.30	−0.13	48.6	18
	Fe^{3+}	0.34	0.84		50
	Fe^{2+}	0.96	1.88		32
12 mm	α-Fe$_2$O$_3$	0.30	−0.16	48.9	19
	Fe^{3+}	0.34	0.76		66
	Fe^{2+}	0.92	1.99		15
15 mm (red layer)	α-Fe$_2$O$_3$	0.30	−0.16	49.0	38
	Fe^{3+}	0.29	0.73		56
	Fe^{2+}	0.96	1.83		6

δ = isomer shift relative to αFe; Δ = quadrupole splitting; ε = quadrupole shift; B_{hf} = hyperfine magnetic field; RA = relative spectral areas

Table 2 80 K ^{57}Fe-Mössbauer parameters for subsamples from different depths along the transected wall of the Tupiguarani ceramic sample of the archaeological Beltrão site

Subsample	Site	δ ($\pm0,0$ 5) mm/s	Δ, ε (±0.05) mm/s	B_{hf} ($\pm0,5$) tesla	RA (±1) %
0 mm (orange layer)	α-Fe$_2$O$_3$	0.48	−0.11	52.1	40
	Fe^{3+}	0.40	0.90		59
	Fe^{2+}	1.12	2.45		1
3 mm	α-Fe$_2$O$_3$	0.47	−0.10	51.8	23
	Fe^{3+}	0.44	0.84		48
	Fe^{2+}	1.09	2.54		30
6 mm	α-Fe$_2$O$_3$	0.46	−0.08	50.9	15
	Fe^{3+}	0.47	0.85		42
	Fe^{2+}	1.08	2.53		43
9 mm	α-Fe$_2$O$_3$	0.41	−0.10	51.0	16
	Fe^{3+}	0.47	0.81		51
	Fe^{2+}	1.10	2.52		34
12 mm	α-Fe$_2$O$_3$	0.47	−0.09	51.1	18
	Fe^{3+}	0.44	0.84		64
	Fe^{2+}	1.11	2.34		18
15 mm (red layer)	α-Fe$_2$O$_3$	0.47	−0.20	52.1	60
	Fe^{3+}	0.44	0.78		37
	Fe^{2+}	1.14	2.36		3

δ = isomer shift relative to αFe; Δ = quadrupole splitting; ε = quadrupole shift; B_{hf} = hyperfine magnetic field; RA = relative spectral areas
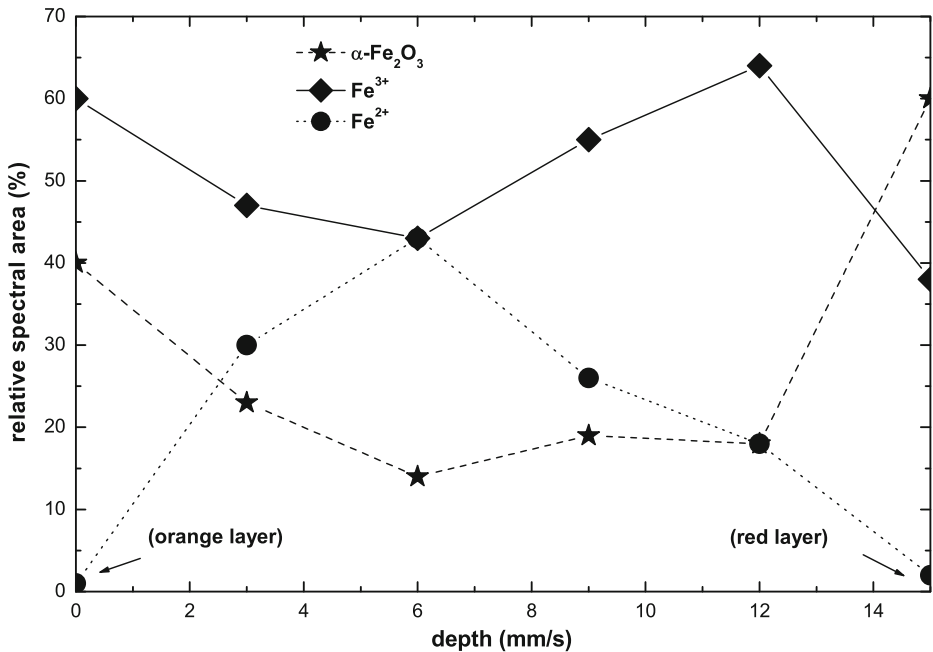
Fig. 8 Breakdown of Fe^{2+} and Fe^{3+}, from Mösbauer spectra for subsamples collected along the section across the transected wall of the ceramic sample from of the archaeological Beltrão site

(Crystallography Open Databases; updated on March 2012) database, through the software Match!® version 2.0.5, by Crystal Impact.

The powder XRD analysis revealed the occurrence mainly of quartz (60,9 %) and muscovite (28.9 %). Some reflection peaks were assigned to rutile (4.0 %), microcline (3.2 %), hematite (1.7 %) and ilmenite (1.2 %). The relative values are in agreement with the semiquantitative analysis performed by the software, based on the parameter I/I_c [3–5]. All subsamples are composed of very small particle sizes, and this tends to make a more reliable identification of other mineralogical phases more difficult.

The spectrum obtained with Mossbauer spectroscopy at room temperature and at 80 K are showed in Fig. 7 and corresponding parameters in Tables 1 and 2, respectively.

Results reveal that hematite is the magnetically ordered phase. The relative subspectral area (RA) for the Fe^{3+} distribution corresponds to between 40 % and 60 %. A ferrous component (RA = 43 %) appears in the central part of the whole spectrum for the grayish layer (Fig. 8). It is likely to be due to some reducing component occurring in this subsample [6–8].

4 Conclusion

From X-ray fluorescence spectroscopy data no significant difference was found for the elemental chemical composition along the transected section, in this archaeo-

logical ceramic sample. The main detected chemical elements, after oxygen, were aluminum, silicon and iron.

X-ray diffraction patterns reveal the main occurrence of two iron oxides: hematite (αFe_2O_3) and ilmenite ($FeTiO_3$).

The red layer is thought to be the external side of the ceramic utensil that had direct contact with fire used to burn the precursor clay in air, during its preparation.

The grayish middle layer has more probably resulted from burning clay mixed with some ashes containing residual carbon, under milder temperature than on the external parts.

Mössbauer data reveal that the orange layer, corresponding to the internal side of what is assumed to be an archaelogical ceramic pot, does contain about the same $Fe^{2+}:Fe^{3+}$ ratio but much lower proportion of α-Fe_2O_3 than the external red layer.

The breakdown of iron chemical states as the $Fe^{2+}:Fe^{3+}$ ratios thorough the transversal section of this pottery piece, as deduced from Mössbauer analyses, may be then taken as a primary evidence of the main conditions, meaning temperature gradient, mixture or direct contact of the precursor clay with chemical reducing agents, like carbon-rich ashes from the burnt wood, and origin and mineralogical nature of the clay itself, used to prepare the ceramic.

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