ARCHEOMETRY RESEARCH ON THE TAQUARI VALLEY

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ABSTRACT

For an archaeometry research project, potteries, soil sediments, clays and other materials have been collected from four archaeological sites in Taquari Valley, Lajeado, state of Rio Grande do Sul (Brazil). In the present paper, the thermoluminescence dating and NAA (Neutron Activation Analysis) and ICP-MS (Plasma Mass Spectrometry) analysis of materials from two of four sites have been carried out. From the site I, ages ranging from 400 to 930 years and from the site II ages from 400 to 1530 years were obtained. From the chemical elements determination of 13 potteries fragments from sites I and II, it was possible to separate them into two groups, such that eight high similarity (90 to 100%) while in the second one five of them had large dissimilarity.

RESUMO

Dentro de um projeto de pesquisa, cerâmicas, sedimentos, solos e demais materiais foram coletados em quatro sítios arqueológicos no Vale do Taquari, Lajeado, localizado no estado do Rio Grande do Sul (Brasil). Neste trabalho foi feita a datação das amostras por termoluminescência e a análise química foi feita empregando-se duas técnicas analíticas NAA (Ativação Neutrônica) e ICP-MS (Espectrometria de massas com plasma) de dois dos quatros sítios. No sítio I, as idades variaram de

400 to 930 anos e no sítio II 400 to 1530 anos. As determinações dos elementos químicos de 13 fragmentos de cerâmicas de ambos os sítios possibilitou a sua separação em dois grupos, um composto por oito amostras de similaridade elevada (90 to 100%) e outro com as cinco amostras restantes com alta discrepância.

Keywords: Archaeometry, Taquari Valley, ICP-MS, NAA,

1. INTRODUCTION

Peopling Southern Brazilian Sates

I. Sambaquis culture

Schmitz (2006) stated that studies of the Brazilian coastal plains are largely related to the so called sambaquis, which are prehistoric deposits of shells, kitchen refuse and skeletons. The people lived in the coastal plain are then called sambaquis society, with a typical sambaquis culture. The southern sea coast in Brazil was peopled by sambaquianes around 3,340 ± 70 years B. P., according to Schmitz (2006).

II. Tupi-Guarani culture

There is another important Indian settlement in southern states of Brazil, that took place much later than sambaquis people. Guarani and Tupi are two large native people of the northern South American continent. They gradually drifted to south. Eventually a part of each group mixed up giving rise to Tupi-Guarini culture.

Particularly, in Jacuri River Valley and Tapuani Valley, radiocarbon dating Brachado (1991) tentatively set following dates intervals for two Tupi-Gurani settlement in these region:

5000 A. D. –	beginning of the settlement
500 - 900 A. D. –	Old period
900 - 1300 A. D. –	Intermediate period
1300 - 1500 A. D. –	Late period.
1500 - 1800 A. D. –	Colonial Period.

2. MATERIALS AND METHODS

Potteries fragments, soil and clay samples have been collected from four archaeological sites in Taquari Valley, Lajeado, state of Rio Grande do Sul for archaeometry investigation.

To start with materials from two of the four sites have been considered for dating and chemical elements components analysis by NAA (neutron Activation Analysis) and by ICP-MS (Plasma Mass Spectrometry). Here soil samples refer to sediments from the place where pottery fragments have been collected. Clays samples did not belong to the same place. Some of them came from the place close to the archaeological sites however, two others have been collected from place 20-25 km from this site.

Each ceramics fragment was cleaned, broken and sprayed, in a dark room, very careful to avoid to triboluminescence effect, and then sieved to retain only the desired grain size. Samples with grain size lower than 0.08mm were separated for chemical analysis by ICP-MS. In this fraction, several elements were determined including potassium, uranium and thorium levels were determined for the subsequent determination of the annual dose rate.

Around 700 mg of sample with size diameter between 0.088 mm and 0180 mm was chemically treated with a HCl solution (37% v/v) for forty minutes in order to eliminate the strange substances in the ceramic tissue. After that, it was treated with a HF solution (10% v/v) to remove surface portion of the grains so that any alpha rays effects are removed. It is important to note that between the chemical treatments the sample was leached with purified water (Ω 18MOhm) to eliminate up completely all the acidity of the medium. The residue was on standby for about 48 hours to dry completely. Then, each sample was split into several aliquots, each of these in amount sufficient for at least five TL readings Each aliquot was then irradiated to γ-doses varying from 5 to 40 Gy, in interval of 10Gy in an irradiator type GAMACELL with dose rate of 2.98 kGy/h (Jan 2007), installed in CTR-Centro de Tecnologia of Radiação - IPEN/SP. Then thermoluminescence measurements were performed using a TL reader (model 110 Daybreak Automatic System), with heating rate of 10^0C/s. After obtaining glow curves, the intensities of 325^0C peak was plotted as function of radiation dose, resulting in a straight line. The extrapolation of this line to the dose axis gives the value of the accumulated dose, D_{ac},, that is to be the radiation dose with which the pottery was irradiated by natural radiation during the time from when it was buried until collected for studies. This procedure to determine D_{ac} is called additive method.

To find the age in which we are interested, it was used the so called annual dise rate, D_{an}, namely the dose-value per year of natural radiation that irradiated the potteries. D_{an} is estimated based on the uranium, thorium and potassium contents given by NAA and/or ICP-MS measurements. If the

concentrations of these elements are given in ppm, using, for instance Table4.5 in the Ikeya (1993) book, it is possible to obtain D_{an} value.

Around 50mg of each dried sample (or certified reference material) was digested in acid mixture solution (nitric acid and fluoridric acid – 5:2) with a closed microwave assisted system (DGT 100 plus – Provecto Analitica) and analyzed using a quadrupole ICP-MS system (ELAN Perkin Elmer 6100). The elements determined quantitatively were Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn. Fe, Co, Ni, Cu, Zn, As, Sr, Zr, Mo, Cd, Ba, La, Ce, Pb, Th and U. The element selection was based on the fact Brazilian soil is rich on silicates and these elements are probably the main components. A robust ICP-MS analytical program was developed and for that, gravimetric reference solutions, prepared from the dilution of each mono-element Spex® stock solution, were used to obtain the individual analytical curves. It was also prepared synthetic matrix solutions to evaluate the matrix effect. A series of four GSJ geological certified reference materials (JG1a, JA-3, JB2 and JB-3) and one soil certified reference material (IAEA Soil 7) were also analyzed to establish the analytical method performance.

For NAA analysis, the ceramic powder samples were obtained by cleaning the outer surface and drilling to a depth of 2-3 mm using a tungsten carbide rotary file attached to the end of a flexible shaft, variable speed drill. Depending on the thickness, 3 or 5 holes were drilled as deep into the core of the sherd as possible without drilling through the walls. Finally, these materials were dried in an oven 105°C for 24h and stored in desiccator.

Constituent Elements in Coal Fly Ash (NIST-SRM-1633b) and Trace Elements in Soil (IAEA-Soil-7), were used as standard and as check samples in all analysis.

In this work, to evaluate the analytical process and establish the chemical elements which can be used in the data interpretation, the elemental concentrations for the reference material IAEA-Soil-7 Trace Elements in Soil were statistically compared with the data found in our laboratory. All possible interference potentially occurring in gamma-ray spectrometry were considered and checked.

3. RESULTS AND DISCUSSION

Figure 1 presents a typical glow curve of powdered pottery fragments.

Figure 2 shows the TL intensity vs dose line, where Dac is shown in the intensities of this line with dose-axis.

Table I gives the ages found for potteries from two sites.

Table II for NAA and Table III for ICP-MS measurements, list main elements determined

In order to establish a pattern using the chemical element determinations, the results were transformed to log to compensate the large differences of magnitudes between the measured elements for the trace level and the larger ones. One reason for this is a belief that, within the raw materials of manufacture, elements have a natural log-normal distribution, and that normality of the data is desirable. Another reason is that a logarithmic transformation tends to stabilize the variance of the variables and would thus give them approximately equal weight in an unstandardized multivariate statistical analysis. All individual determinations in each data set were tested for discordant results. The Mahalanobis distance, Di, is suggested by many authors as a method for detecting outliers in multivariate data. The data treatment by hierarchical cluster analysis with the squared Euclidean distances was used to calculate dissimilarities between samples. Figure 3 shows the dendogram obtained as result of these calculations.

Figure 3 shows it was possible to separate them into two groups, indicating probably a different aw materials origin for each group.

4. CONCLUSIONS

The TL dating carried for RST 110 corrugado (I) and RST 110 (II) indicated these sites have been occupied around 1500 years BP, however, living people in these sites remained there until 400 years BP. The collected potteries fragments are visibly from different periods , once they were found in different depth in the underground.

In the resulting dendrogram were evidenced the distinct groups of samples that have different chemical composition. So, it was possible to separate them into two groups, such that eight high similarity (90 to 100%) while in the second one five of them had large dissimilarity.

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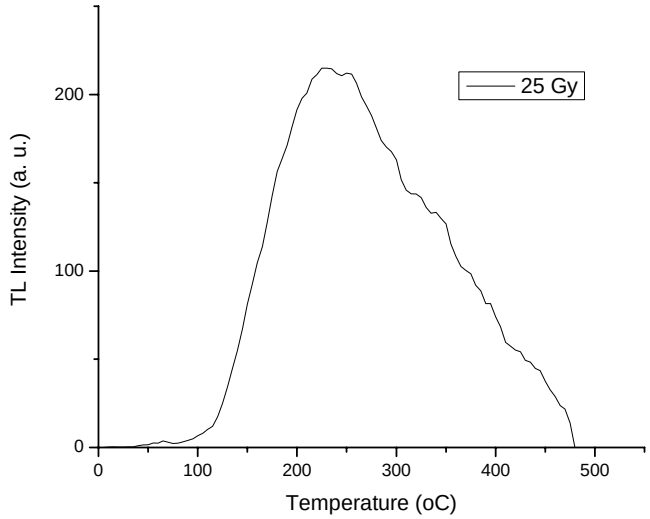

Figure 1. TL Glow Curve of 2290 Pottery Fragment irradiated with γ-dose of 25 Gy

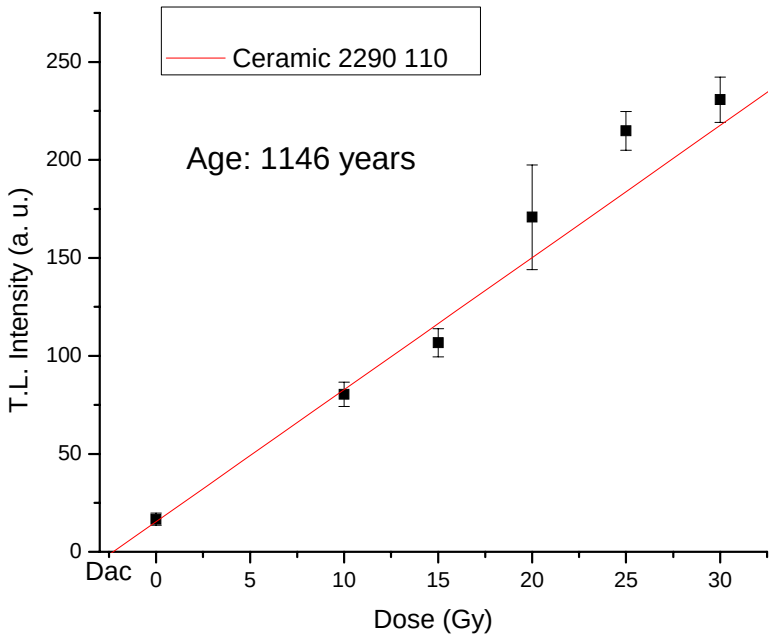

Figure 2. TL Intensity vs Dose for 2290 Pottery Fragment.

Table I. Ages Determined by TL Method

RST 110 Corrugado		RST 110	
Ceramic	Age (Years)	Ceramic	Age (Years)
3751	385 ± 20	2277	362 ± 20
2364	558 ± 30	3753	548 ± 30
2439	606 ± 35	3766	725 ± 40
1558	630 ± 30	2279	988 ± 40
1559	926 ± 50	2290	1146 ± 50
		2272	1528 ± 65

Table II. Chemical Composition obtained by NAA analysis

Sample	2279	2277	2272	3766	2858	3757	3739	2290
Na (%)	0.5	0.1	0.4	0.4	0.3	0.5	0.5	0.4
K (%)	2.1	0.5		2.6	9.2	1.8	1.6	
Fé (%)	5.3	2.9	5.9	5.1	5.2	5.9	5.5	6.4
La (ppm)	41.9	38.9	45.5	56.1	38.8	47.2	59.9	50.4
Sm (ppm)	8.5	6,00	14.7	10.5	10.7	9.1	11.1	15.1
Yb (ppm)	3.7	2.7	6,00	4.6	3.7	4.1	4.8	4.2
Lu (ppm)	0.7	0.6	0.6	0.7		0.7	0.7	0.7
U (ppm)	4.9	2.4		4.1	3.6	4.1	4,00	
Sc (ppm)	24.4	25.6	24.7	28.1	23.3	24.1	26.2	23.5
Cr (ppm)	42.3	125,00	39.2	55.6	74.4	44.2	40,00	45.3
Co (ppm)	19.1	33.6	16.8	17.8	30.2	21.6	18.7	36.2
Cs (ppm)	8.9	7.2	3.3	8.7	7.3	10.2	11.1	6.6
Ce (ppm)	73.1	75.5	77.4	86.6	60.4	95.7	93.7	113.7
Eu (ppm)	1.7	1.8	1.6	2.3	1.6	1.9	2,00	2.1
Tb (ppm)	2.1	0.5	1.5	1.7	1,00	1.5	1.6	
Hf (ppm)	9.3	5,00	6.6	8.4	8.6	7.6	9,00	7.6
Ta (ppm)	1.6	0.8		1.9	1.3	1.4	1.8	
Th (ppm)	15.3	6.4	15,00	15.2	12.3	14	15.2	17.7

Table III. Chemical Composition (% mass) obtained by ICP-MS analysis

Sample	1558	1559	2439	2364	3751
Mn (%)	0.32	1.06	0.44	0.26	0.32
Fe (%)	33.51	36.22	27.01	7.54	9.36
Al (%)	8.63	14.21	15.54	18.01	10.70
Ca (%)	4.49	1.41	7.39	0.85	3.50
K (%)	6.62	7.13	8.37	1.24	4.86
Ti (%)	1.45	1.81	2.85	1.04	1.49
Mg (%)	4.82	5.77	5.85	0.08	3.78
Na (%)	0.30	0.31	0.08	0.22	0.53
Cr (ppm)	57.48	93.49	89.49	86.23	316.76
V (ppm)	107.80	271.30	92.04	173.02	265.87
Ni (ppm)	7.06	14.71	34.01	14.32	31.55
Zn (ppm)	78.73	598.99	114.97	563.31	878.34
Pb (ppm)	2.13	6.50	19.41	2.75	10.87
Li (ppm)	44.54	114.92	56.41	146.39	83.44
Cu (ppm)	79.07	131.06	7.40	111.39	150.73
La (ppm)	71.00	157.98	17.92	191.87	124.09
Ce (ppm)	35.07	141.11	46.61	218.70	63.53
Th (ppm)	44.31	96.39	25.02	109.17	83.60
U (ppm)	1.22	0.87	0.69	0.09	1.75
Sr (ppm)	216.97	126.09	342.39	160.64	91.54
Zr	126.42	296.66	68.64	409.11	184.20

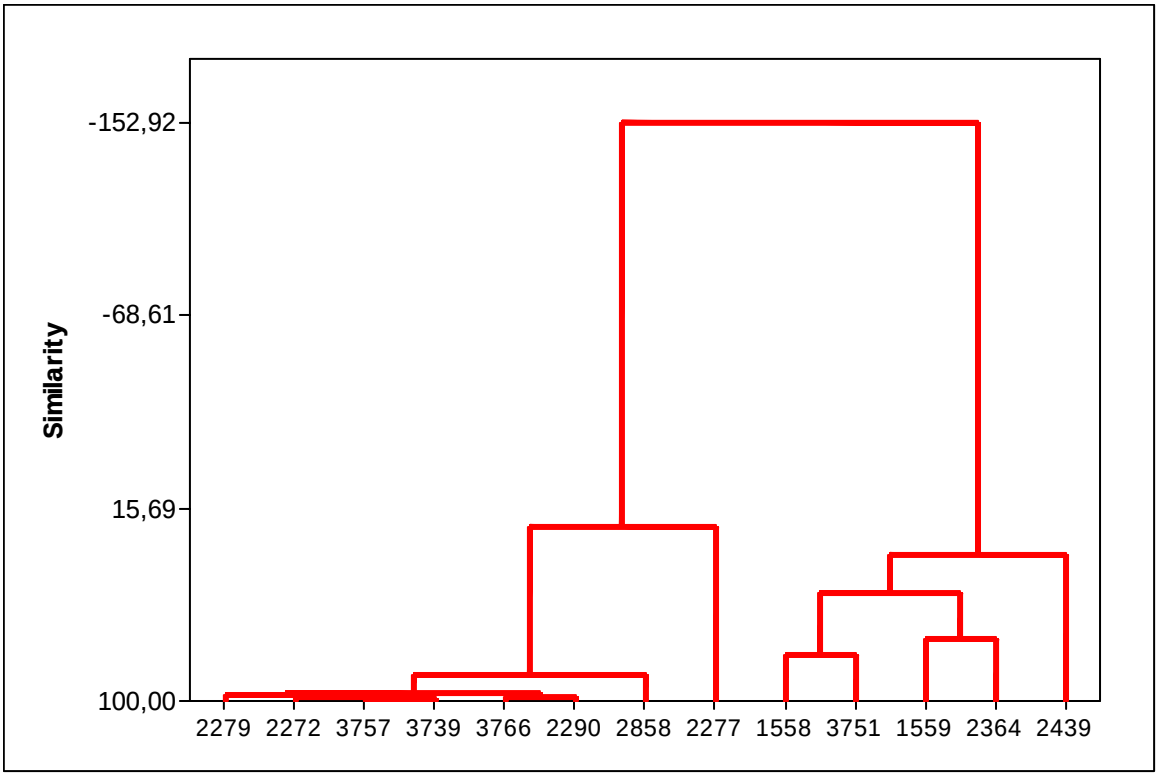

Figure 3. Dendogram of Studied Pottery Fragments;