

A provenance assessment of ancient pottery through instrumental neutron activation analysis at the Monte Castelo site, Rondônia, Brazil

Patricia R. Carvalho¹, Casimiro S. Munita¹, Eduardo G. Neves², Carlos A. Zimpel²

¹Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP), Av. Professor Lineu Prestes 2242, 05508-000 São Paulo, Brazil

²Museu de Arqueologia e Etnologia da Universidade de São Paulo, Av. Professor Almeida Prado 1466, 05508-070 São Paulo, Brazil

ABSTRACT: This research aims to contribute to the discussion of ceramic objects found at the Monte Castelo shell mound (*sambaqui*), an archaeological site located at south-west Amazonia, Brazil. The first study performed in the area in the 1980s suggests that this archaeological site is inserted within one of the oldest contexts of ceramic production in Amazonia. Until today, there have not been any studies of the physical and chemical properties of these objects to reconstruct clay procurement practices and contribute to their archaeological interpretation. With this purpose, this paper provides the results of a preliminary chemical characterization of eighty-four pottery samples using instrumental neutron activation analysis (INAA) by means of the determination of Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Rb, Sc, Sm, Th, U, Yb and Zn. The compositional analysis produced substantial geochemical data that allowed comparisons of the similarity/dissimilarity between the samples by means of cluster, principal components and discriminant analysis. The results showed the existence of three different chemical groups whose dates range from 3,000 B.P. to 1,500 B.P. and are in agreement with other studies that place the Bacabal phase as the oldest ceramist culture in the Southwest of the Amazon. Additionally, this study provided a solid research framework of investigation that can be employed for more detailed and extensive future studies on ancient human occupation in the research area.

Keywords: Archaeometry, pottery, instrumental neutron activation analysis, Amazonia, Provenance analysis.

1. Introduction

Globally, pottery fragments are the most common type of artifact found in archaeological sites due to their high resistance to physical–chemical soil conditions. Their macroscopic characteristics such as decoration, color, form and function are cultural and chronological indicators in archaeology (Lima 2011). However, ceramics can be also examined in terms of mineral and chemical composition, and this information can be useful for better understanding of some cultural aspects (Glascock & Neff). These studies are based on the assumption that the ceramics of the same production series are chemically and mineralogically similar within a particular site or area of manufacture (Weigand et al 1997).

There are several modern analytical techniques that can be employed to determinate the chemical composition of archaeological ceramics. However, among the analytical methods, INAA employing γ -ray spectrometry seems to be the most suitable over other techniques because all problems related to the decomposition of the sample and separation are avoided. This aspect is very important when unique or valuable materials, like archaeological and artistic objects must be analyzed. In addition, is also possible the determine several elements simultaneously with high sensitivity, precision and accuracy (Dias & Prudêncio 2007, Glascock et al 2004, Hossain et al 2015, Munita 2005).

This research aims to clarify ceramic provenance in south-west Amazonia by means of INAA chemical characterization of ceramic fragments from the Monte Castelo shell mound. In order to establish the age of the samples the TL technique was used. In summary, this article provides new insights on the development of ceramic production in the Amazonia region through compositional analyses of the Bacabal phase ceramic assemblage from this site.

The direct relevance of this archaeometric study relates to the capability of establishing the provenance of the ceramics retrieved at the Monte Castelo, which in turn illuminates issues of human occupation and cultural variability in the region.

1.1 Archaeological framework

The Amazon basin is the largest and most complex terrestrial ecosystem. Since its area includes nine Latin American countries, due to its large size, it has often been seen as a demographic void (Mongeló 2015, Roosevelt 1992). However, archaeological research in the region has shown a very different picture. Archaeological remains found in different areas indicate a deep and complex history of human occupation. With this perspective, some archaeological currents concentrate on the search of traces of human occupation to prove that before the arrival of the Europeans to the continent, the Amazon was dense and diversely occupied (Neves 2013).

In the Amazon, the older contexts of pottery production are always associated with shell mound *sambaquis*. The Monte Castelo shell mound is one of the oldest contexts of pottery production in the Amazon and is located in the alluvial plain of the Branco river, about 20 km from its confluence with the Guaporé river (Miller 2009).

The first archaeological studies at the site were made by Miller in the 1980s, who found large quantities of ceramic fragments, lithic artifacts, plant remains, and abundant faunal remains, including snails of the genus *Pomacea* that constitute the matrix of the shell mound (Miller 2009).

The 22 dates obtained by ^{14}C allow the reconstruction of a sequence of cultural development that began with a long pre-ceramic occupation of ca. 8400 years ago named the Cupim phase, followed by the Sinimbu phase from ca. 7,100 B.P. and the Bacabal phase ca.4,000B.P.(Miller 2009). Unfortunately Miller was unable to continue his work due to an attack of malaria and could not return to the excavate.

2. Materials and methods

This section is divided in two different subsections that detail the methods and techniques applied in this study. We begin by outlining the chemical characterization applied to the archaeological ceramics, then we describe the analytical process applied to determine the age of the samples.

2.1. INAA methodology

INAA is a nondestructive method that does not require complicated handling and where the problems related to losses and sample contamination are avoided. In general terms, in this procedure the standard

containing a known quantity of elements of interest is irradiated together with an unknown sample. The principle of the method is given elsewhere (Dias & Prudêncio 2007, Glascock et al 2004, Hossain et al 2015, Munita 2005, Weigand et al 1997).

A total of 84 ceramic samples were analyzed. The external surface was removed with a fine bristle brush. After that, holes were made on the samples with a tungsten carbide rotary file, attached to a variable speed drill. Around 500 mg of powdered sample were obtained from three to eight holes on the side surface of the ceramic fragment, preventing the drill from crossing over the walls.

The powder was dried for 24 h in an oven at 104 °C and stored in desiccators (Munita 2005). Approximately 100 mg of each sample were weighed in polyethylene involucres and sealed with sealing iron. Groups of up to seven ceramic powdered samples and two reference materials were wrapped in aluminum foil. The Standard Reference Material – NIST - SRM 1633b was used as standard and the IAEA Reference Material, IAEA-Soil 7 Trace Elements in Soil, was used for the analytical quality control.

The samples and the standards were irradiated in the swimming pool research reactor IEA-R1 of the Nuclear and Energy Research Institute, IPEN-CNEN/SP, at a thermal neutron flux of about $1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ for 8 h. The measurements were carried out using a Ge (hyperpure) detector, model GX 2519 from Canberra, with a resolution of 1.90 keV at the 1332 keV gamma peak of ^{60}Co . The spectra were collected by a Canberra S-100 MCA with 8192 channels on an automated sample changer. The gamma-ray spectra analysis and the concentrations were carried out using the Genie-2000 NAA Processing Procedure from Canberra. Two measurement series were carried out. The elements Na, K, La, Sm, Yb, Lu and U were measured after 7 days of decay. The elements Sc, Cr, Fe, Co, Zn, Rb, Cs, Ce, Eu, Hf and Th were measured after 25–30 days of decay (Baria et al 2015).

2.2. TL dating method

Dating by the TL (thermoluminescence) technique uses the naturally occurring decay of U, Th and K in soil where a ceramic is buried to determine its age. The TL intensity of natural samples is proportional to the absorbed dose up to dating. In the case of ceramics, the ionic crystals are

the quartz grains contained in the clay from which the ceramics are made. The zeroing of the archaeological clock is defined by the moment the clay mould is heated to high temperature to produce ceramics (Aitken 1985, Bartool & Ikeya 1997, Mckeever 1985). The accumulated dose (D_{ac}) is determined from the ratio TL_{ac}/TL_0 where TL_{ac} is the TL value obtained from a given mass of quartz grains and TL_0 is the TL emitted by annealed quartz grains of the same mass. Finally, annual dose rate (D_{an}) is calculated from measurements of the radioactive elements within the material and its surroundings where the pottery was collected and from the radiation dose rate from cosmic rays. The age of the pottery can be calculated by the D_{ac} divided by the D_{an} .

To obtain the pure quartz grains from each sample to determine the D_{ac} approximately 1mm of surface layer was removed by sawing with a diamond grinding wheel. After that, the material was carefully crushed in an agate mortar, dried and sieved. The powder with diameter between 0.080 and 0.0180 mm was subjected to chemical treatments with H_2O_2 30%, HF 20% and HCl 20% solutions to corrode a thin layer of the surface of quartz grains in order to clear the surface and to eliminate the possible presence of α -particle effects, carbonates and organic matter and separate the quartz as best as possible (Baria et al 2015).

The quartz grains were used for TL measurements using multiple aliquot regeneration, MAR, procedure assuming that the sensitivity to the laboratory radiation was the same as it had been for radiation during burial (Aitken 1985, Bartool & Ikeya 1997, Mckeever 1985).

The regenerative dose samples were then warmed from room temperature to a final temperature of 500 °C with a heating rate of 5 °C/s remaining at 200 °C for 10 s to erase the TL signal from the peaks of low temperatures that are very unstable (Aitken 1985, Bartool & Ikeya 1997, Mckeever 1985). The TL measurements were performed using a Risø TL/OSL Luminescence Reader Model TL/OSL DA-20 equipped with a $^{90}Sr/^{90}Y$ β radioactive source with a dose rate of 0.081Gy/s.

The annual dose value was estimated from uranium, thorium and potassium concentrations obtained by INAA (Dias & Prudêncio 2007, Glascock et al 2004, Hossain et al 2015, Munita 2005, Weigand et al 1997).

3 Results

One of the basic premises underlying the use of chemistry in ceramic provenance analysis is that clay sources can be differentiated if an adequately precise analytical technique is used. If an element is not measured with good precision it can obscure real differences in concentration and the discriminating effect of other well-measured elements tends to be reduced. These differences can be used to form ceramic compositional groups because vessels manufactured from a given clay source will be more similar to each other than to other vessels manufactured from a different source (Baria et al 2015).

In this work, the precision of the analytical method was studied using the reference material IAEA-Soil 7, for which 14 independent determinations were made. Table 1 shows the radioisotope, the energy used in the analysis, the mean, standard deviation (SD), the relative standard deviation (RSD) and the confidence interval. The results found were compared with the certified values.

In the table, the RSD values are in agreement with the values recommended. However, in this paper we only use elements with RSD less than 10% for the interpretation of the results. This precision is considered appropriate by several authors for the choice of the chemical elements for studies of archeological objects using multivariate statistical methods (Bishop et al 1990). Although Co had RSD 4.37, it was eliminated from the data set because its concentration can be affected by tungsten carbides files during sample preparation (Attas et al 1984).

Results indicate that U precision was affected by the experimental conditions adopted and would need to be determined using epithermal NAA, ENAA. The measurement of zinc via ^{65}Zn using the peak of 1115.55 keV, $T_{1/2} = 245$ d is hardly possible in geological materials using INAA due to the strong influence of ^{46}Sc with energy 1120.5 keV and $T_{1/2} = 83.9$ d, ^{182}Ta and ^{152}Eu with a gamma peak in 1112.0 keV. Furthermore the precision Yb determination via ^{175}Yb using the peak of 396.32 keV and $T_{1/2}=101$ h was affected by the energy of 398.2 keV from ^{233}Pa . Lastly the interference of ^{235}U fission in the determination of La and Ce was negligible because the U concentration did not exceed 5 ppm and the rare earth elements were not extremely low (Glascock 1992).

Therefore, the elements Na, K, La, Sm, Sc, Cr, Fe, Cs, Ce, Eu and Th were used in subsequent data analyses.

Table 2 shows the range, the mean and the standard deviation for elemental analyses of the 84 ceramic samples investigated in the present study. None of the elements considered contained missing values.

Previous authors (Harbottle 1982) have differed over whether mass fraction data for geological materials are distributed normally or lognormally. Ahrens (Beier & Mommsen 1994, Koch & Link 2002) has noted, if the dispersion in the data is small compared to the mean mass fraction, the lognormal distribution approximates a normal distribution. In this work the data set was rescaled to base10 logarithms because the assumption of lognormality is also convenient, the log transformations compensating for the large differences in magnitude between the high-concentration elements, such as Na, K and Fe, and the trace elements. Then, log transformation creates a convenient quasi-standardization or rescaling of the original data that facilitates the application of various multivariate methods (Oliveira & Munita 2003). Details on the calculations and reasoning behind these transforms can be found elsewhere (Popelka-Filcoff 2007).

After logarithmic transformation the data set was submitted to outlier tests. Many multivariate methods are sensitive to outliers and it is convenient to identify and remove them before analysis. The quadratic Mahalanobis distance matrix between each sample coordinates vector and the mean vector was calculated using the Statistic software. The values were compared with the lambda Wilk's critical value for the identification of multivariate outliers (Oliveira & Munita 2003). Only two samples were considered an outlier and were removed of the data set.

A preliminary classification of the data set was made with hierarchical cluster analysis, HCA, to outline possible clusters or groups within the elemental data. This was performed with the program R using as similarity measure the squared Euclidean distance among the mass fraction of 11 elements and the linking criterion used was the Ward's method. The grouping that resulted from chemical analysis of the sample is presented in the dendrogram in Figure 1. The result of the cluster analysis outlined the separation of the samples into three very well-defined groups, henceforth referred to as Groups 1, 2 and 3, containing 44, 18 and 20 samples, respectively.

After identifying the chemical groups by HCA, a principal components analysis was also performed to evaluate the samples in the data set that

contribute to the variance (Hazenfratz et al 2016). Figure 2 shows the PC1 vs PC2 and PC3. The three PCs explained 72,54 % of the total variance. Figure 2 shows that the samples cluster together in three groups in agreement with cluster analysis and with technological and stylistic characteristics.

A discriminant analysis was carried out in order to verify and confirm the data structure. The basis for all multivariate analyses is that all the elements included are independent variables. This is not necessary true, but it can be tested using the pooled within-groups correlation matrix provided by discriminant analysis (Koch & Link 2002). Figure 3 shows discriminant function 1 vs discriminant function 2. As can be seen, each group forms a chemical relatively homogeneous showing a degree of chemical similarity among themselves.

These results clearly showed that compositionally the pottery samples are discriminated in by at least three centers of production, that may be identified in the area. Whether these sources are local or not will only become clear in other work by means of a systematic local analysis.

The chemical groups are in agreement with the stylistic diversity of whole vessels found at the site that were studied by means of techno typological method. The compositional data were able to reinforce the group divisions made stylistically and suggests the likelihood of at least three production locations of the pottery from Monte Castelo. With the purpose to see if the samples are from the same period, two samples of each group were submitted to TL analysis for dating.

From the stylistic point of view, the diversity within the three compositional ceramic groups suggest that the samples would be from different time periods. In this case, the compositional data would serve to reinforce the group divisions based on style and indicate several production events.

Table 3 shows the results for the accumulated dose and annual dose, both in uGy, and the age of the samples in years.

As can be seen in Table 3, the ages of the samples vary according to the groups. The samples of the first group are the oldest and their ages vary from 2,408 to 3,220 years B.P

For samples of group 3 the ages range from 1,446 to 1,523 years B.P. However, the ceramics from group 2, range in age from 1,859 to 1,947 years B.P. The age of the ceramics of the three groups are in agreement

with previous archaeological chronologies that place the Bacabal phase from ca. 3,000 years B.P. extending to 1,500 years B.P (Miller 2009).

Conclusion

The compositional variation exposed by the chemical analysis of ceramics from the Monte Castelo archaeological site suggested the likelihood of not one but rather of three occupations that are in agreement with typological studies made in the site. From the stylistic point of view, the three compositional ceramic groups show style diversity and suggest that the samples would be from different time periods that was confirmed by means of the age of the phases that ranged from 1,446 to 3,220 years B.P. in agreement with the Bacabal phase in the region, the compositional data were able to reinforce the group divisions made stylistically and indicate three production events in the site.

In conclusion, this research provides a solid framework of investigation that can be employed in the future to carry out more detailed and extensive study at Monte Castelo shell mound. It is likely that further archaeometric analyses based on high-resolution compositional technique (INAA) on archaeological materials from Amazonia will help to clarify networks of cultural interactions in the future.

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Captions for Tables and Figures

Table 1: Results for IAEA Soil 7 determinations in mg/kg, unless otherwise indicated, n= 14.

Table 2: Range, mean and standard deviation for ceramic samples from Monte Castelo archaeological site in mg/kg, unless otherwise indicated.

Table 3: Accumulated dose, D_{ac} , annual dose rate D_{an} and age obtained.

Figure 1: Dendrogram of 84 samples from Monte Castelo archaeological site using Ward's method and squared mean Euclidean distances.

Figure 2: 3D principal component analysis

Figure 3: Discriminant function 1 vs. discriminant function 2

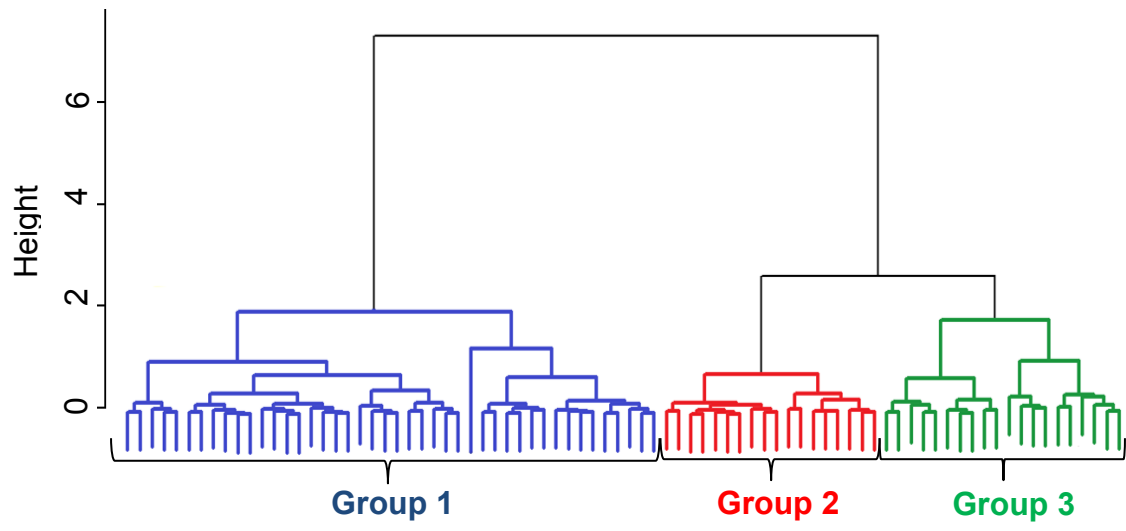


Fig. 1

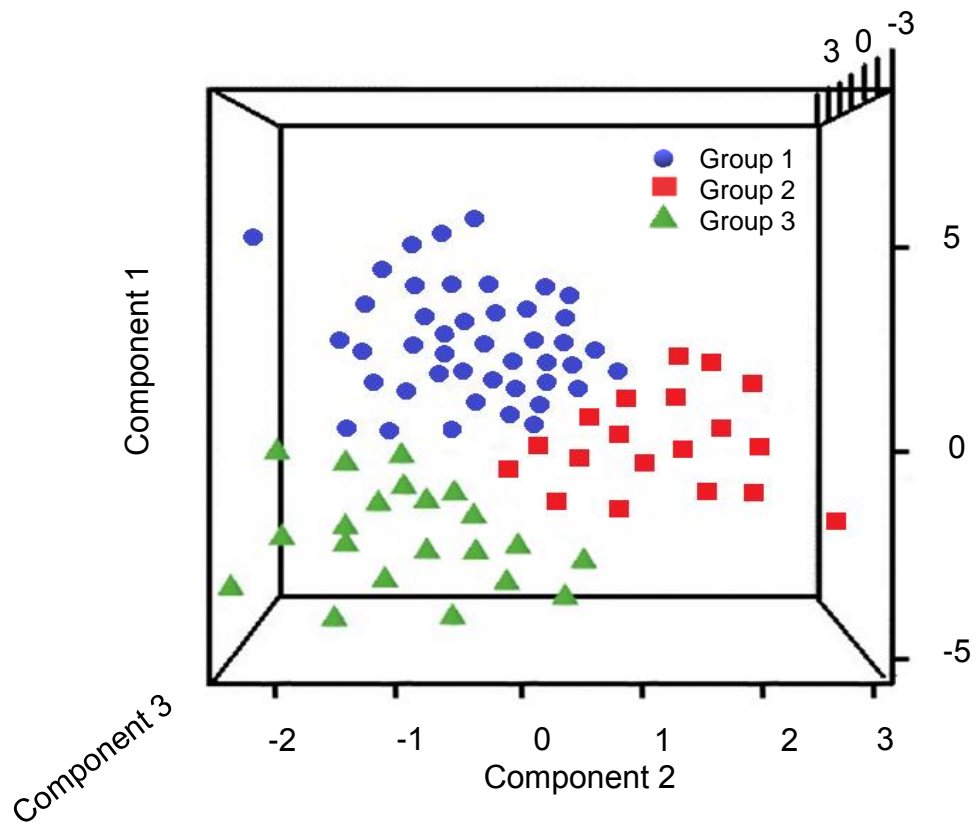


Fig. 2

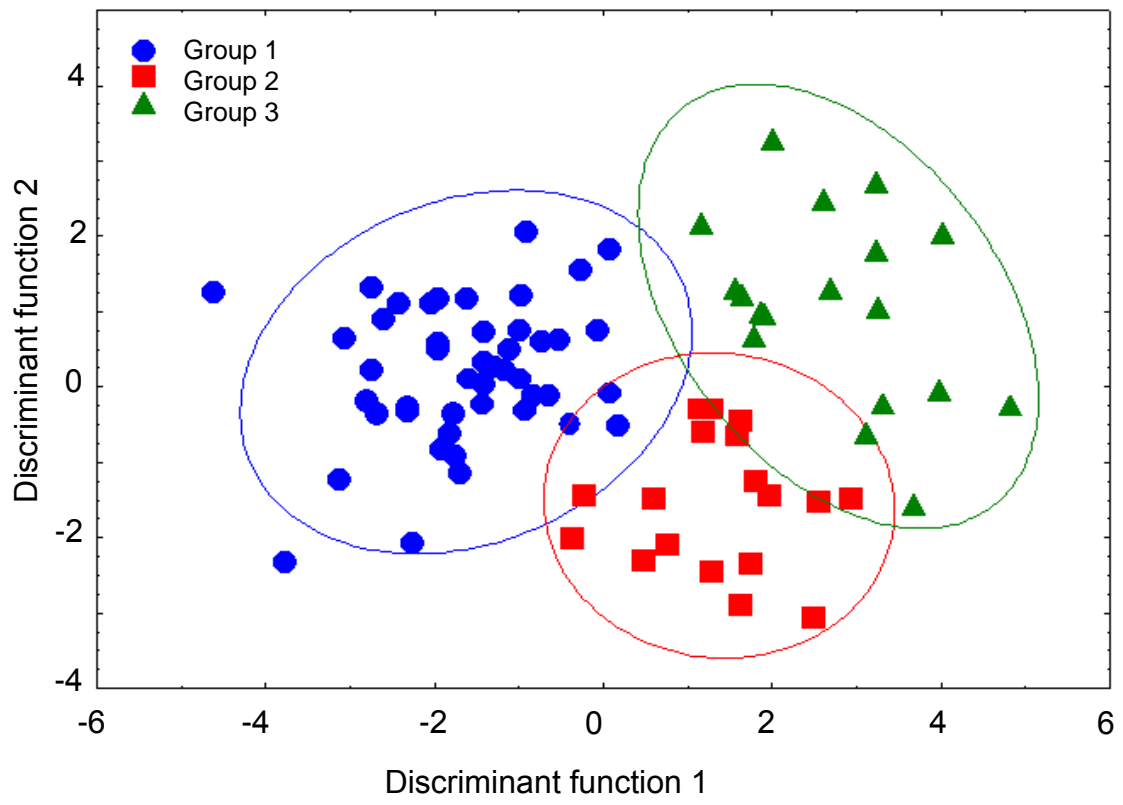


Fig. 3

Table 1

Element	Certified value	Mean \pm SD	RSD (%)	Confidence interval
Na (g/kg)	2.40	2.35 \pm 0.08	3.54	(2.30 – 2.50)
K (g/kg)	12.10	12.39 \pm 0.70	5.62	(11.30 – 12.70)
La	(28)	30.81 \pm 0.88	2.87	(27.00 – 29.00)
Sm	(5.1)	5.59 \pm 0.27	4.77	(4.80 – 5.50)
Yb	(2.4)	2.29 \pm 0.29	12.55	(1.90 – 2.60)
Lu	0.3	0.36 \pm 0.04	10.47	(0.10 – 0.40)
U	(2.6)	2.45 \pm 0.64	26.32	(2.20 – 3.30)
Sc	(8.3)	8.71 \pm 0.19	2.14	(6.90 – 9.00)
Cr	(60)	68.74 \pm 4.14	6.02	(49.00 – 74.00)
Fe (g/kg)	(25.7)	26.08 \pm 0.72	2.75	(25.20 – 26.30)
Co	(8.9)	9.11 \pm 0.40	4.37	(8.40 – 10.10)
Zn	(104)	93.03 \pm 13.29	14.29	(101.00 – 113.00)
Rb	(51)	60.50 \pm 13.72	22.69	(47.00 – 56.00)
Cs	(5.4)	4.97 \pm 0.21	4.19	(4.90 – 6.40)
Ce	(61)	60.19 \pm 0.99	1.64	(50.00 – 63.00)
Eu	(1)	1.02 \pm 0.10	9.94	(0.90 – 1.30)
Hf	(5.1)	5.06 \pm 0.60	11.90	(4.80 – 5.50)
Th	(8.2)	8.19 \pm 0.51	6.24	(6.50 – 8.70)

Table 2

Element	Range	Mean \pm SD ^a
Na, mg/g	0.31 - 1.45	0.71 \pm 0.28
K, mg/g	5.11 - 21.07	10.89 \pm 2.83
La	14.75 -57.91	34.05 \pm 9.26
Sm	2.72 -25.25	6.74 \pm 3.50
Sc	6.36 - 18.67	12.16 \pm 2.54
Cr	30.44 -76.73	51.87 \pm 11.21
Fe, mg/g	9.47-30.07	16.60 \pm 4.92
Cs	2.16 - 12.44	5.17 \pm 2.03
Ce	30.39-117.36	63.62 \pm 19.93
Eu	0.391 - 2.04	1.06 \pm 0.38
Th	5.70 - 16.74	10.37 \pm 2.43

^aMean and standard deviation of 84 individual samples

Table 3

Group	Sample	D_{an} (μGy)	D_{ac} (Gy)	Age (years B.P.)
1	1	1,767 ± 122	5,69 ± 0,15	3,220 ± 238
	2	2,197 ± 168	5,29 ± 0,06	2,408 ± 186
2	3	2106 ± 159	4,10 ± 0,10	1,947 ± 154
	4	2,862 ± 190	5,32 ± 0,20	1,859 ± 142
3	5	3,153 ± 135	4,56 ± 0,096	1,446 ± 69
	6	2,804 ± 156	4,27 ± 0,073	1,523 ± 89