ATD

A NOTE ON THE DIFFERENTIAL THERMAL ANALYSIS OF AMAZONIAN ARCHEOLOGICAL POTTERY †

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INTRODUCTION

Studies by Mössbauer spectroscopy (M.S.) of archeological pottery suggested that the alterations observed in samples of different ages in the iron oxides may be connected with hydration processes in the pottery(1)(2). Similarly, it has been suggested that the weathering of baked sediments and its effects on archeomagnetic measurements are a consequence of physico-chemical processes leading to the presence of hydrated iron minerals in such sediments(3)(4).

Kingery(5) has shown that differential thermal analysis (DTA) can be a useful tool for the study of hydration processes in some archeological pottery.

In the present work we investigate by DTA sherds of archeological pottery of the mouth of the Amazon river. These samples have been previously investigated by thermoluminescence (T.L.)(6) and M.S. and our aim has been to establish possible correlations between the hydration phenomena and the observed changes in the iron oxides of the pottery.

EXPERIMENTAL

Samples from the Meggers and Evans collection(7) of the Museu Nacional (Rio de Janeiro) and of Museu Emilio Goeldi (Belém Pará) were selected for investigation.

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These sherds were collected in several sites of the island of Marajõ, at the mouth of the Amazon river. They correspond to five archeological phases, some of which were previously dated by C-14 and more recently by TL[6].

Semi-quantitative spectrographic analysis of several samples corresponding to the different phases showed that their composition, based on the results for 32 elements, is remarkably similar. The oldest pottery, from the Ananatuba phase (about 3.000 years old), contains in general less concentration of elements as compared to the more recent ones.

In a previous study with thin sections of the samples it has been established from the presence of carbonaceous (bitumeous) residues in the ceramic matrix that the firing temperature was less than 700-800°C[6].

The samples were cut and after removal of the external parts they were crushed in a mortar and sieved. The 200 mesh fraction was selected for measurements. About 20 mgs of material is placed in the vacuum chamber of the instrument, which removes its surface humidity. The spectra were recorded at a temperature rate of 8°C/min. up to 800°C.

RESULTS

Fig. 1 reproduces the spectrum obtained with an Ananatuba sample. With all samples the same type of spectra is observed. The three curves recorded simultaneously by the instrument correspond to the increase in temperature (T), the thermogravimetric variations (Tg) and the differential thermal spectrum of the sample (DTA).

The region between 90°C to 130°C exhibits a defined endothermic peak. It is followed by a not well defined exothermic region which extends up to 800°C. At higher temperatures an ill-defined endothermic process occurs.

Fig. 2 reproduces the DTA endothermic peak recorded for the samples investigated around 100°C.

The area of the peak has been determined according to Mackenzie procedure[8]. Table 1 lists the results obtained together with the known ages of the samples. For the first group of samples listed in Table 1, TL ages and C-14 dates from charcoals of the same stratigraphic levels are available (6). For a second group of samples, the ages were calculated from the TL archaeological dosis taking the average value of the annual radiation dosis measured with 12 other samples.

DISCUSSION

In a pioneer work Grim and Bradley[9] have shown that clays fired at temperatures below 800°C gradually become rehydrated and very slowly regain their original structure. For example, montmorillonite heated 1 hr at 600°C reformed about 25 per cent of the original crystal lattice water in 268 days.

In connection with these results, the X-rays studies by L. Courtois[10] have shown the presence of smectic clay minerals in ancient pottery. Together with the DTA by Kingery, these results indicate that archeological ceramic samples originally fired in the temperature range below 700-800°C reacquire characteristics of the unfired clays over long periods of time.

We have confirmed the presence of regenerated illite chlorite in all our samples by X-ray measurements.

In pure clay minerals the rehydration process occurs simultaneously as a physical process of picking up water molecules and a chemical one which leads to the recovery of lattice water hydroxyl groups. The DTA spectra show two endothermic peaks, the first around 100°C and a second one around 500°C. It is only the first DTA peak which is present in the spectra of the ancient potteries.

This suggests that it is mainly a physical process of reacquiring the water molecules which is the slow process occuring in the ancient potteries. The presence of a well defined transition around 100°C corresponds to the removal of interlayer water between the silicate sheets*. The interlayer water is structurally organized and its growing process is analogous to that of a crystal growth[11]. It is the slow growing rate of the structural water which determines the kinetics of the rehydration process of the clay minerals in the ancient potteries. On this basis one can explain the observed correlation between the size of DTA peak corresponding to the release of structural water and the age of the potteries.

It is possible that this correlation holds particularly well for the Amazonian archeological pottery due to the similar

* It is important to distinguish between the physically adsorbed water on the surface of the clay minerals and the interlayer water[11]. Water molecules on the first situation are easelly removed at in an extended temperature range below 100°C whereas the complete removal of interlayer water requires a well defined energy.

composition of the samples; relatively low firing conditions, and permanent humidity of environment at a quite stable temperature.

As a consequence of the slow rehydration of the clay minerals the iron oxides in the archeological pottery, such as hematite and magnetite, will gradually turn to hydroxides, such as goethite or lepidocrocite. The size of the originally present magnetic iron oxide particles in thus reduced. This can explain the observed decrease in aged samples of the magnetic fraction present at a given temperature in the Mössbauer spectrum of the pottery and the deviation from linearity of the Thellier's plots in archeomagnetic measurements of baked sediments.

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REFERENCES

1 - Kostikas A., Simopoulos A. and Gangas N.H., 1976, Analysis of Archaeological Artifacts, in Applications of Mössbauer Spectroscopy, Vol. 1, Ed. R.L. Cohen, Academic Press, New York.

2 - Danon J., Enríquez C.R., Mattievich E. and Beltrão Maria da C.M.C., 1976, Mössbauer Study of Aging Effects in Ancient Pottery from the Mouth of the Amazon River, J. Phys., Colloque C6-866.

3 - Barbetti M.F., McElhinny M.W., Edwards D.J. and Schmidt P.W., 1977, Weathering Processes in baked sediments and their Effects on Archaeomagnetic Field intensity measurements, Phys. Earth Planet. Int., 13, 346-354.

4 - Sigalas I., Gangas N.H.J. and Danon J., 1978, Weathering Model in Paleomagnetic Field Intensity Measurements on Ancient Fired Clay, Phys. Earth Plan. Int., 16, 15-19.

5 - Kingery W.D., 1974, A Note on the Differential Thermal Analysis of Archaeological Ceramics, Archaeometry, 16 (1),109-112.

6 - Courtois L., Beltrão M. da C.M.C., Danon J., Reyss J.L., Valladas G., Simões M.F. and Valladas H., 1978, Thermoluminescent Dating of Archeological Pottery from the Marajó Island (Brazil), Fifth International Conference on Luminescence Dosimetry, São Paulo, Brazil, pag. 459-468.

7 - Meggers B.J. and Evans C., 1957, Archaeological Investigations at the Mouth of the Amazon River - Bull. Bureau Amer. Ethnol., 167, U.S. Gobernement Printing Office, Washington.

8 - Mackenzie R.C. (Editor), 1957, The Differential Thermal Investigation of Clay, Mineralogical Society, London.

9 - Grim R.E. and Bradley W., 1948, Rehydration and Dehydration of the Clay Minerals, Amer. Min., 33, 50-59.

10 - Courtois L., 1973, Phénomènes de régénération aprés de cuisson de certaines céramiques anciennes, C.R. Acad. Sc. Paris, 276, D-2931-2933.

11 - Grim R.E., 1968, Clay Mineralogy, Mc Graw Hill, pag. 314.

TABLE 1

CERAMICS	AGES (B.P.) TL	C-14	PEAK AREA Relative Units
Marajoara 48	630 ± 70	1260 ± 200	86
Marajoara 161	1730 ± 200	1470 ± 200	261
Ananatuba 79	3060 ± 270	2930 ± 200	437
Mangueira 69	3040 ± 270	2930 ± 200	317
Ananatuba 78	3410 ± 300	2930 ± 200	421
Piratuba s/n	600		91
Piratuba 88	800		57
Marajoara 8300	1000		147
Marajoara 140	1000		164
Marajoara 160	1200		160
Ananatuba 47	3000		
Ananatuba 33	3000		
Ananatuba 34	3400		

FIGURE CAPTIONS

Fig. 1 - Differential Thermal Analysis (ATD) curve and Thermogravimetric curve (TG) of Ananatuba archaeological sample from the Marajó Island.

Fig. 2 - Differential Thermal Analysis endothermic peak observed around 100ºC in several archaeological potteries of different ages from the mouth of the Amazon River.

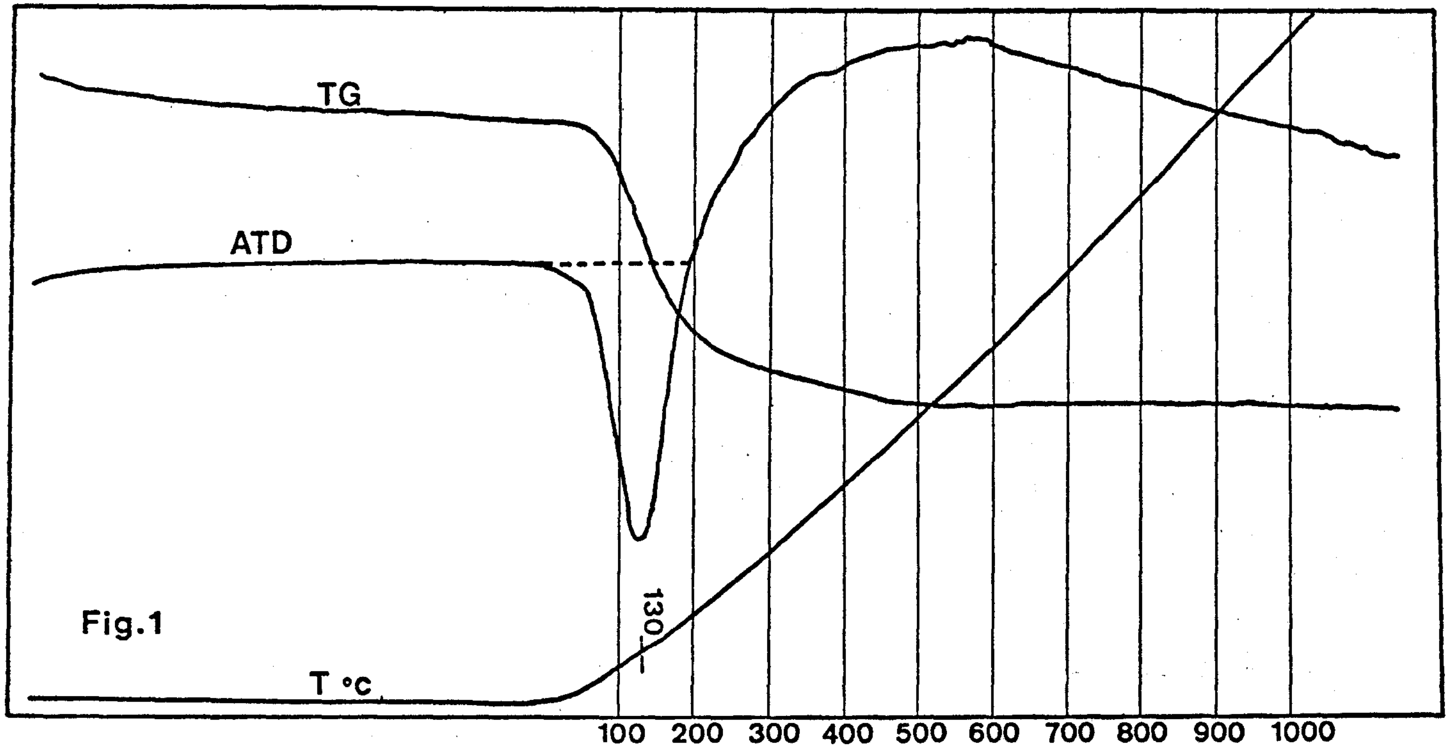
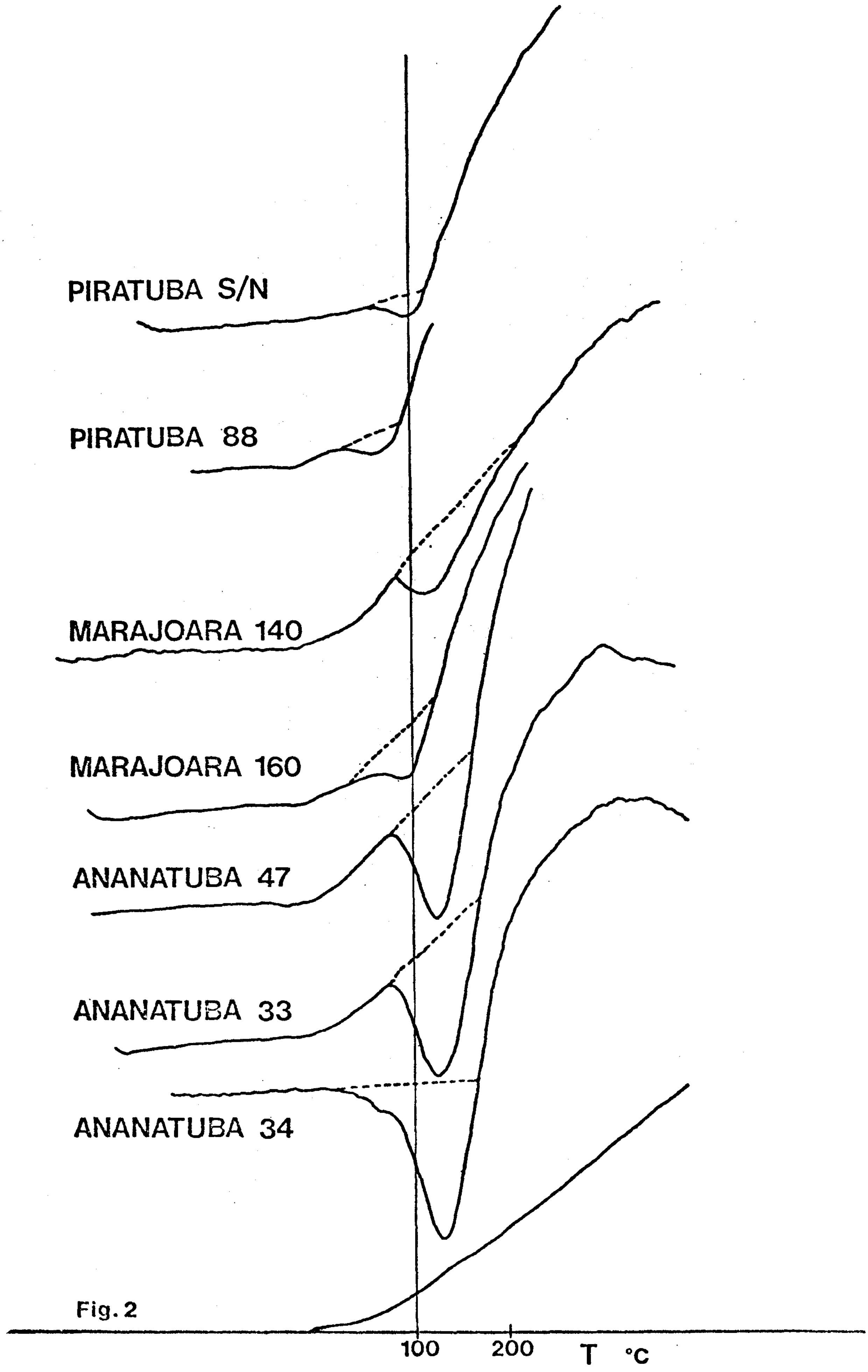


Fig.1



PIRATUBA S/N
PIRATUBA 88
MARAJOARA 140
MARAJOARA 160
ANANATUBA 47
ANANATUBA 33
ANANATUBA 34
100
200
T °C

Fig. 2