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RETHINKING ABOUT CHRONOLOGY OF CHICHEN ITZA: BY THERMOLUMINESCENCE DATING OF VOLCANIC GLASS

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ABSTRACT

One of the most frequently recurring questions in archaeology concerns the age of the studied objects. To date, determining the chronology of the Puuc and Chichen Slate pottery of Chchen Itza, based on the stylistic change in the pottery, has been problematic. The Thermoluminescence method of dating pottery was applied to samples of Chichen Itza, Yucatan, Mexico, which contain volcanic glass as temper. They were analyzed using the fine grain technique. The radisotopes that contribute to the accumulate annual dose in ceramic samples (^{40}K, ^{238}U, ^{232}Th) were determined by means of Energy Dispersive X-ray Spectroscopy and Neutron Activation Analysis technique, while the artificial irradiation of the samples was carried out using ^{90}Sr source beta radiation. We obtained results indicating the following dates; 875 ± 88; 1055 ± 85; 1063 ± 47, 1154 ± 76; 1110 ± 53, 1132 ± 69, 1221 ± 30, 1532 ± 26. The results demonstrate a chronological order of dates. Most results are in accordance with the established dates of Chichen Itza. However, Puuc and Chichen Slate did not show differences of 200 years as previously proposed, and there is evidence of an earlier period than those two pottery periods. This necessitates a reconsideration of the chronology of Chichen Itza.

KEYWORDS: chronology, Chichen Itza, pottery, volcanic glass, thermoluminescence dating, fine grain technique

INTRODUCTION

Chichen Itza is the most famous ruin of *Post-classic Mayan* civilization. Ancient *Mayan* civilization developed in the areas known today as Mexico, Guatemala, Honduras and Belize. The development of Mayan civilization is divided into three periods: *Preclassic, Classic,* and *Post-classic*. As the most developed *Classic Mayan* period decayed around 900 A.D, some Mayans migrated further north to Chichen Itza, in the north of the Yucatan peninsula in Mexico. From that time Chichen Itza developed as a foreign and seperate group, named Itza. They flourished during the next 200 years of the Post-classic period. However after 200 years, this group returned to their homeland and Chichen Itza began to decline (Morley,1987; Piña Chan, 1987).

Over the last 60 years archaeologists determined the chronology of Chichen Itza based on the stylistic changes of pottery which are a result of the cultural layer sequence. Specially two types of pottery styles were used to distinguish between the Classic and Postclassic periods of Chichen Itza. *Puuc Slate Ware* represents the *Classic* period, 800 to 1000 A.D, before the arrival of foreigners, whereas *Chichen Slate Ware* represents the *Postclassic* period 1000-1200 A.D., the development period after the arrival of foreigners (Smith,1977).

However, from the very beginning when this chronology was first established, the archaeological evidence of the cultural layer and the chronology based on the stylistic change of pottery were not always matched correctly. (Tozzer,1957; Brainerd,1958). For this reason, a more precise method of dating is necessary to determine the chronology of Chichen Itza. If we could estimate the fabrication date of the *Puuc and Chichen Slate Ware*, we would be able to determine more precisely the *Classic* and *Post-classic* periods of Chichen Itza.

Thermoluminescence(TL) is the emission of light when a substance is heated under its incandescence temperature. The TL emitted by the minerals in a pottery sample was produced by the prolonged exposure to the ionizing radiation emitted by the radioisotopes ^{238}U, ^{232}Th, and ^{40}K embedded in the sample as impurities, and from the surrounding soil. Cosmic rays also contribute fractionally to the TL signal. The accumulated dose is named *Paleodose(P)*. Radiations can be found in concentrations of a few parts per million (ppm) and have a very long *half-life (*between 10^9 and 10^{11} years). Therefore, the amount of TL induced is proportional in time from the moment of firing of the pottery to the time when the TL intensity is checked. Increased temperature to fire the pottery completely eliminates the TL obtained during the geological time and sets the clock to zero. This means that we can count chronometry from the moment the pottery was fabricated. Therefore *thermoluminescence (TL)* dating could be an adequate method to determine the fabrication dates of the *Puuc* and *Chichen Slate* pottery.

METHODOLOGY

1. Selection of samples from test pits.

Pottery fragments were collected from all cultural layers of the 13 test pits of the archaeological site of Chichen Itza. The stratigraphy of Chichen Itza's test pits conserve the cultural period sequence in order (Chung 2000: 101). Fragments of pottery were collected at every cultural layer in the test pits. They were then classified by visible and tactic characteristics, such as *Puuc Slate*, *Chichen Slate*, and others.

Pottery fragments collected from test pits were not washed and were immediately saved on black plastic containers, protected from heat and sunlight, and kept at the field laboratory. There, all sherds were washed and dried naturally in a cool and shaded location. Next, sherds were selected that were big enough (4-5 cm each side) for analysis, from every cultural layer and every test pit. After 2-4 weeks, all selected samples were delivered to the laboratory of Geophisics of National University of Mexico.

2. Selection of samples by Petrographic Thin Section analysis

The samples were cut into very thin layers of 30μm in order to analyze the minerals by petrographic thin section study. The results of this study enabled us to divide all samples into two groups. The first group of pottery contained carbonate as temper and the second group con-

tained *volcanic glass shards* as temper. It is possible to use TL estimates on either carbonate or volcanic glass. However, since we eliminated carbonate for cleaning we selected samples that contain volcanic glass shard to date. Finally, 8 pottery fragments of *Slate Ware* were selected from different *cultural layers*.

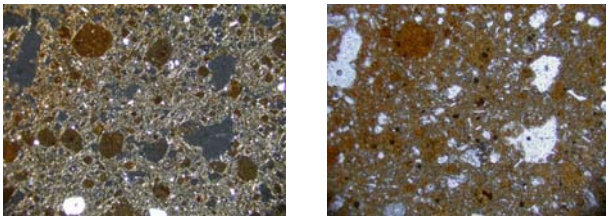

Fig. 1. Microscopic images of Chichen Slate Ware:

The left image was taken by crossed nicole; the right image, by open nicole. Volcanic glass, biotite, rock fragmensts, hematite, and clay lumps are visible. Volcanic glass is identified as black shards in the left image and transparent in the right image. The size of the shard is 0.007-0.17 mm. 90X

3. Determination of Annual dose and Paleodose

The annual dose was estimated with natural radioisotopes (^{40}K, ^{238}U, and ^{232}Th), and *cosmic contribution*. The paleodose was estimated by the *additive* and *regenerative* methods of calculating the *equivalent dose* and *supralinearity factor* respectively. Once obtained the paleodose and annual dose were substituted into the age equation:

$$Age = \frac{Paleodose\,(Q+I)\,(Gy)}{Annual\ Dose\ Rate\,(Gy/y)}$$

Where Q: Equivalente dose, I: Supralinearity factor and Annual dose rate (ADR): alpha, beta, gamma and cosmic contribution dose.

To estimate the annual dose rate, the ^{40}K concentration was determined by means of energy dispersive spectroscopy (EDS). Meanwhile, the ^{238}U and ^{232}Th contents were obtained by means of the neutron activation analysis (NAA) technique, using the Triga Mark III reactor operating at 1 MW. These analyses took place at the National Institute of Nuclear Research of Mexico. The cosmic contribution (gamma radiation) dose rate was measured using locally made LiF: Mg, Cu, P+PTFE TL dosimeters (González, 2007).

For determination of Paleodose, the technique applied was the *fine grain method* (Zimmerman, 1971). A 2 mm layer was removed from all pottery sample surfaces. Then the sample was crushed in an agate pestle and mortar. The fine grains between 4-11 μm were separated from coarse grains by sinking them into acetone solvent. The collected fine grains were treated with H_2O_2 to remove the organic materials and with HCl to neutralize the carbonates.

More than 60 discs, each carrying 2 mg of the sample, were prepared to check the ability to reproduce the procedure. Discs were made of aluminum substrate 0.5 mm thick and 9 mm in diameter. The preparation and analysis of samples was formed under the red light illumination. TL readings were carried out at the Geophisics Institute of UNAM using the Daybreak 1100 automated TL analyzer. This system is equipped with a sample-holder which can carry 20 samples, and it is coupled to a PC Pentium loaded with software to control the process. Beside the function of adjusting the hardware system, the software permits the analysis of the *plateau* (region of interest) and uses the least squares fitting of the growth curves to give an estimate of the dose equivalent (Q) and the supralinearity correction factor (I).

The dose equivalent (Q) was determined by the *additive method.* Artificial irradiation of the samples was made with a ^{90}Sr-^{90}Y, β source of Amersham with an activity of 3.7 GBq giving a dose rate of 185 Gy/h. After irradiation, samples were stored in the dark, and the TL readings were taken 15 days later. No variation in TL intensity was observed during this storage period. Data taken into account was from the discs whose readings exhibited an uncertainty of less than 4%. This suggests that the sample does not undergo anomalous fading.

Determination of factor (I) was carried out by means of the *regeneration method*. The natural TL curve of each sample was confirmed previously. Each of these samples were divided into 16 separate discs and irradiated to regenerate a new TL curve. In each study, samples were irradiated in groups of 4 discs at a time. Four artificial doses of 1 β, 2 β, 3 β and 4 β were given in

vacuum. If we graph the doses against the *TL intensity*, we will obtain a calibration curve which determines the correction factor of *supralinearity (I)*.

RESULTS

Table 1 shows the amount of ^{40}K, ^{238}U and ^{232}Th concentrations, the moisture contribution and the annual dose rates in mGy y^{-1} of each sample. The average gamma radiation received from soil and cosmic rays was 0.36 ± 0.01 mGy y^{-1}. Taking an α efficiency factor of 0.10 and a Th/U ratio of 3:1 (Adamiec, 1998), annual dose rates in dry conditions were obtained.

Table 1. Concentration of ^{40}K, ^{238}U, and ^{232}Th, moisture and annual dose (A.D. mGy y-1) of each sample

Sample	K (%)	U (ppm)	Th (ppm)	Moisture (%)	A.D. (mGy/y)
CH11	1.26 ± 1.01	4.85 ± 0.07	32.06 ± 3.21	18.84	5.32 ± 0.19
CH13	2.76 ± 0.80	3.79 ± 0.06	13.12 ± 0.16	18.22	4.44 ± 0.13
CH14	2.79 ± 0.71	2.18 ± 0.05	16.39 ± 0.20	16.34	4.25 ± 0.15
CH15	2.64 ± 1.24	1.36 ± 0.04	22.53 ± 0.28	14.79	4.44 ± 0.18
CH16	2.34 ± 1.20	2.17 ± 0.33	20.07 ± 1.71	15.07	4.31 ± 0.15
CH17	2.54 ± 0.97	2.02 ± 0.04	13.85 ± 0.22	14.03	3.93 ±0.02
CH18	2.43 ± 1.72	1.93 ± 0.03	13.65 ± 0.21	17.44	3.64 ± 0.03
CH19	2.45 ±0.78	2.40 ± 0.13	22.00 ± 3.77	15.92	4.55 ± 0.24

Figure 2 shows the plateau test. We can observe an increasing factor from 200ºC and form a plateau between 290-310ºC, in which it is possible to evaluate the parameters within a high confidence level (Aitken, 1985).

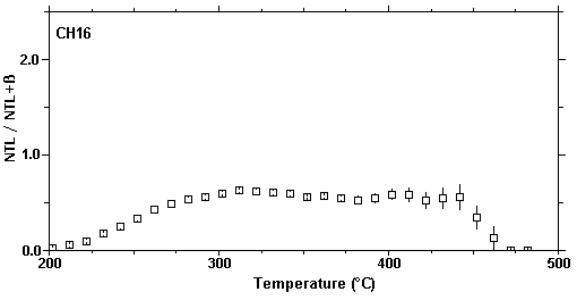

Fig. 2. Plateau test of CH16 shows the stable region between 290-310ºC.

Figure 3 shows the glow curves of unirradiated samples (NTL) CH16 as well as those irradiated with ^{90}Sr beta radiation at four different doses (NTL+nβ). The irradiation dose of beta were 1ß=3.5 Gy, 2ß=7.5 Gy, 3ß=10.5 Gy and 4ß=14.0 Gy. The dose responded calibration curves obtained by *additive method*.

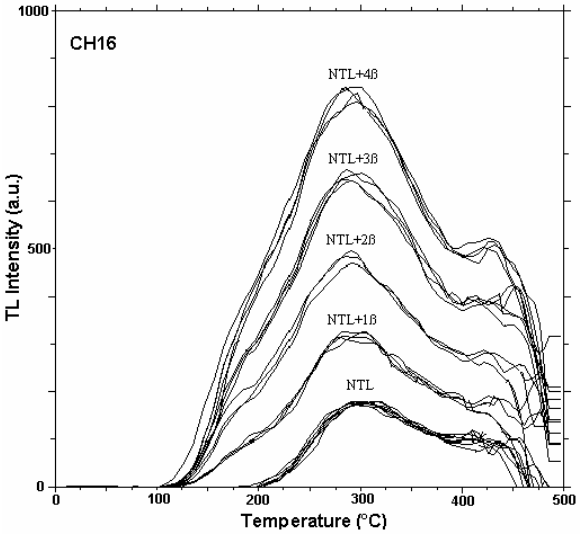

Fig. 3. Glow curves of CH16 both unirradiated (NTL) and irradiated at four different doses (NTL+nß), 1ß=3.5 Gy, 2 =7.5 Gy, 3ß=10.5 Gy and 4ß=14.0 Gy.

Figure 4 demonstrates how calibrated glow curves interpolated to zero TL intensity (TL=0) gives the dose equivalent (Q). Dose equivalent (Q) was determined at every 10°C temperature intervals in the range from 250 up to 400°C for the CH16 sample.

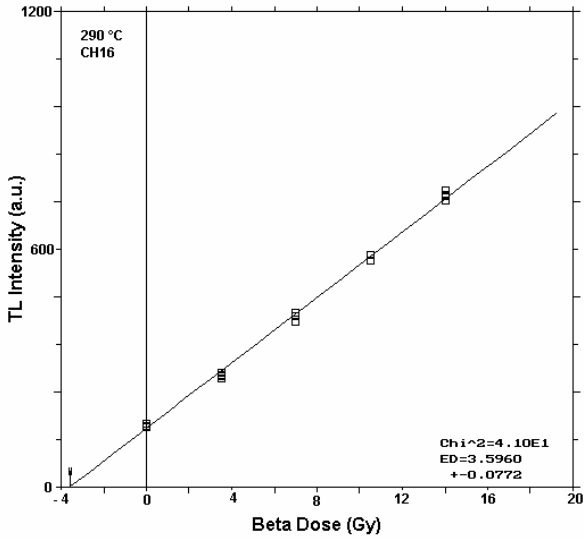

Fig. 4. Equivalent dose Q of CH16

The correction factor due to *supralinearity* was determined by means of the *regeneration method* at the same 10 °C temperature intervals. These results are shown in figures 5 and 6 respectively.

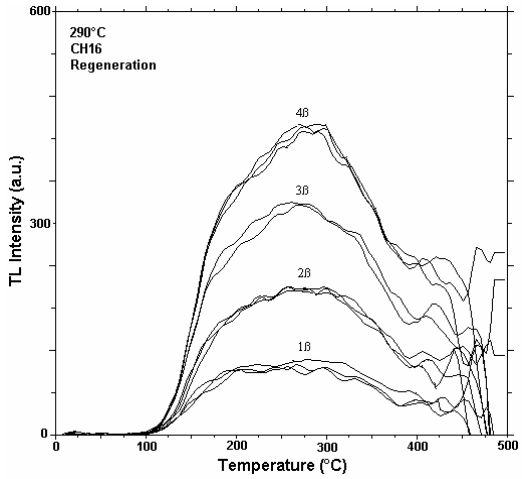

Fig. 5. Regenerated growth curves of CH16, irradiated at the same dose,), 1ß=3.5 Gy, 2 =7.5 Gy, 3ß=10.5 Gy and 4ß=14.0 Gy.

Figure 6 shows regenerated growth curves determine the *supralinearity* factor (I) with the same 10°C temperature intervals.

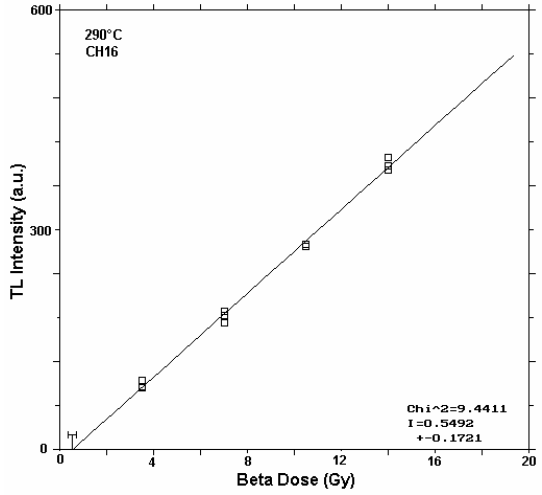

Fig. 6. The *supralinearity* correction factor I of CH16, irradiated at nß

The equivalent dose (Q) plus supralinearity factor (I) determine the Plaeodose. Table 2 shows the result of Q and I, and total amount of Paleodose.

Table 2. The equivalent dose (Q), supralinearity factor (I) and total amount of paleodose (P)

Sample	Q (Gy)	I (Gy)	P (Gy)
CH11	3.19 ± 0.03	1.77 ± 0.15	4.97 ± 0.15
CH13*	1.26 ± 0.04	0.80 ± 0.09	2.07 ± 0.10
CH14	2.23 ± 0.03	1.55 ± 0.03	3.78 ± 0.04
CH15	3.19 ± 0.08	0.66 ± 0.04	3.85 ± 0.09
CH16	3.59 ± 0.17	0.50 ± 0.32	4.09 ± 0.36
CH17	2.79 ± 0.08	0.29 ± 0.01	3.08 ± 0.04
CH18	3.75 ± 0.20	0.36 ± 0.39	4.11 ± 0.32
CH19	2.89 ± 0.17	0.95 ± 0.31	3.84 ± 0.35

The obtained Paleodose and annual dose are substituted into the age equation and the result shown in table 3.

Table 3. The annual dose, the Paleodose and the age obtained by the Age equation.

Sample	A.D. (mGy/y)	P (Gy)	Age (y), B.P.	Converted to A.D.
CH11	5.32 ± 0.19	4.97 ± 0.15	934 ± 47	1063 ± 47
CH13*	4.44 ± 0.13	2.07 ± 0.10	466 ± 26	1532 ± 26
CH14	4.25 ± 0.15	3.78 ± 0.04	889 ± 53	1110 ± 53
CH15	4.44 ± 0.18	3.85 ± 0.09	867 ± 69	1132 ± 69
CH16	4.31 ± 0.15	4.09 ± 0.36	949 ±85	1055 ±85
CH17	3.93 ±0.02	3.08 ± 0.04	784 ± 99	1221 ± 99
CH18	3.64 ± 0.03	4.11 ± 0.32	1129 ± 113	875 ± 113
CH19	4.55 ± 0.24	3.84 ± 0.35	844 ± 76	1154 ± 76

DISCUSSION AND CONCLUSION

It is the first try to apply *Thermoluminescence* dating to mayan pottery. The aim of this investigation was: TL dating is useful to establish chronology of mayan civilization and if so, what kind of pottery could be useful.

Table 4 shows the final dates determined for the pottery of Chichen Itza and a comparison to archaeologically estimated dates.

Table 4. Comparison of TL date and archaeologically estimated date

Sample	Slate Type	Date by TL (AD)	Estimated date (AD)
CH11	Puuc	1063 ± 47	800-1000
CH13*	Chichen	1532 ± 26	1000-1200
CH14	Chichen	1110 ± 53 .	1000-1200
CH15	Chichen Slate	1132 ± 69	1000-1200
CH16	Early Chichen	1055 ± 85	unknown
CH17	Chichen	1221 ± 30	1000-1200
CH18	Tintin	875 ± 88	unknown
CH19	Puuc (?)	1154 ± 76	800-1000(?)

We can observe a chronological order of dates; Tintin Slate (CH18), 875 ± 88; Early Chichen Slate(CH16), 1055 ± 85; Puuc Slate (CH11, CH19), 1063 ± 47, 1154 ± 76; and Chichen Slate (CH13, CH14, CH15, CH17), 1110 ± 53, 1132 ± 69, 1221 ± 30, 1532 ± 26. The results demonstrate that among the four samples of Chichen Slate Ware, 3 samples show dates very close to previously estimated dates. As well we identified a date earlier than the *Puuc* and *Chichen Slate* periods.

When comparing the results of TL dating and previous chronological dating, it is impor-

tant to note that most results are in accordance with the established dates of Chichen Itza. However, the two Slate Wares did not show differences of 200 years as has been commonly accepted. *Puuc* and *Chichen Slate* showed almost the same age. This provides additional evidence of possible problems with the current chronology of Chichen Itza. Another important result is the presence of pottery from an eariler period than the *Puuc* and *Chichen Slate* periods as shown by sample CH18. This suggests that Chichen Itza must have a longer history than was known previously. All of the above demonstrate the necessity to reconsider the chronology of Chichen Itza.

All samples show definite plateaus in their respective graphs as observed in CH16, except CH13. CH13 which has an estimated date of 1532±32 did not show a definite plateau on the glow curve. Since Mayan civilization did not continue to exist in Chichen Itza after 1519, we think CH13 was not an adequate sample for the TL dating method.

According to petrographic thin section results, samples CH11, CH16 and CH18 which demonstrate the most obvious plateaus on the graph, contain mostly volcanic glasses as temper in the reduced matrix paste. Meanwhile CH 15 contains both carbonate and volcanic glass in the oxidized paste. Since carbonate was eliminated during the preparation process, besides the quantity of volcanic glass, the only difference lies in the firing condition of the pottery. Frequently the oxidized paste represents a lower firing temperature than the reduced paste.

As a result, the reduced paste has a more even fire distribution than the oxidized one. To conclude, equal distribution of fire and the presence of termoluminescence mineral like volcanic glass make TL dating of pottery successful.

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