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# Radiation in archaeometry: archaeological dating

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# Abstract

Crystalline inclusions contained in ceramics act as thermoluminescent dosimeters, the irradiation source being the natural radiation environment. Because of this, various ceramic materials (pottery, bricks, cooked clays, bronze claycores) have been dated by thermoluminescence (TL). A short review of the main possibilities of TL dating is given, with some examples that enlighten the advantages and limits of this method in the field of archaeological dating, compared to TL dating of buildings. The assessment of the chronology of Valdivia culture (Ecuador), based on a three-year project of TL dating, is presented and discussed. The overall uncertainty at around 4-5% can be considered the best limit presently available. The uncertainty distribution found among 700 archaeological TL datings and for about 500 building TL datings is also presented. © 2001 Elsevier Science Ltd. All rights reserved.

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#### 1. Introduction

One of the most frequently recurring questions in archaeometry concerns the age of the studied objects. To-date, while existing methods have not been successful in providing dating for all types of material, the presence of the natural radiation environment has been of great help in finding mechanisms on which many dating techniques are based.

The continuous irradiation from naturally occurring radioisotopes and from cosmic rays causes the filling of electronic trapping levels in non-metallic materials. These types of material can, in principle, be dated through the analysis of these filled electronic traps, provided that the manufacturing of the object to be dated coincides with the initiation of the filling of the traps.

This condition is satisfied in the case of thermoluminescence (TL) dating, which in principle can be applied to all materials whose manufacturing requires high temperature heating, typically including all kinds of ceramics, but also bricks, burnt flints, porcelain, cooked hearths and bronze clay-cores.

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The main fields of application of TL dating are in the study of architectural history, through the analysis of bricks, and in archaeology.

#### 2. Basis of thermoluminescence dating

The possibility of dating ceramic objects by the use of their TL properties was first proposed by Grogler et al. (1960) and Kennedy and Knopff (1960), and then extensively studied by the group at Oxford University headed by Martin Aitken (Aitken et al., 1964; 1968). We refer to Aitken's books (1985, 1990) for a thorough analysis of TL dating. Here, we aim to present the basis of TL dating, limiting this to the extent that it should enlighten the reader to its potential, its limits and the sources of uncertainty.

Dating by TL is a particular application of TL dosimetry in which there is a source of constant irradiation, the natural radioactivity of the ceramics, the activity of which can be independently determined. The duration of irradiation is taken to be the same as the age of the ceramic, and this is proportional to the amount of the TL signal. Of course, it is essential to have an initial "zeroing of the TL signal", this generally being provided by the making of the ceramic itself, the high

temperature reached by the furnace during the manufacture of the object erasing the previous TL signal by emptying all of the electronic traps. We stress this point because in some cases, ceramics, during their manufacture, were not cooked at high enough temperature for trap emptying, as in for instance by sun heating or by placement over a fire. In these cases, the period of irradiation does not coincide with the age of the ceramics and the results of TL dating will be incorrect.

In the case of TL dating, ceramics can be considered to consist of a number of crystalline inclusions (mainly quartz and feldspar) embedded in the ceramic matrix. The inclusions act as dosimeters of the irradiation arising principally from the natural radioactivity (U and Th series and <sup>40</sup>K) of the ceramic material. This natural radioactivity is the source of the "internal dose-rate", given by alpha and beta irradiation, which, in a typical ceramics, is responsible for around the 80% of the total absorbed dose. The remaining "external dose-rate" is given by the environmental gamma rays and by cosmic rays. It is then possible to determine the total amount of dose-rate by measuring the concentrations of natural radioactivity of the ceramics and the level of environmental irradiation. Conventional techniques for radioactivity measurements and new dosimetric techniques, specifically designed for TL dating are used.

The total dose absorbed since the making of the ceramics is obtained through TL dosimetry of the crystalline inclusions. Various methods of measurement of the total absorbed dose have been studied, of which the main ones, the so-called *fine-grain* (Zimmermann, 1971) and *inclusion* (Fleming, 1970) techniques, consider grains of different sizes extracted from the ceramics. Also, in these measurements, important dosimetric aspects relative to the absorption of radiation of different kinds (alpha versus beta and gamma) are to be taken into account. We refer again to Aitken's books for further details.

As a conclusion, we summarise the way for obtaining TL ages by the simple *age equation*:

Age = palaeodose/dose-rate,

where the *palaeodose* is the total absorbed dose with respect to the last heating at high temperature. It is calculated from a comparison between the "natural" TL, that has been produced by the irradiation due to natural radioactivity, and the "artificial" TL induced by laboratory irradiation with artificial sources, whose strength is known.

### 3. TL dating in archaeology

From what has been presented in the preceding section, a few conclusions can be drawn regarding the

possible applications of TL dating:

- 1. A relatively large number of measurements are necessary (TL dosimetry of crystalline inclusions, artificial irradiation, radioactivity and dosimetric measurements). As a consequence, to reduce statistical uncertainties, it is useful to collect a large amount of material to be dated.
- Even if most of the irradiation comes from the ceramic itself, the contribution from the environment must be known if uncertainties are to be minimised.

The availability of large quantities of material and a good knowledge of the surrounding environment can easily be achieved when dating buildings, where many important results have been reached. Archaeological dating, which at a first glance could appear as the main field of application of TL Dating due to the world-wide presence of pottery in excavations, must be treated with great care if an accurate evaluation of the environmental dose-rate is to be obtained.

To illustrate the application of TL dating in archaeological contexts, we will describe a typical case of a deep stratigraphic excavation site (the chronology of Valdivia culture, Ecuador), a borderline application to non ceramic material (the clay-cores of bronzes), and a case whose apparently anomalous results gave instead an appreciable contribution to historical and archaeological research.

The Valdivia culture of coastal Ecuador, one of the oldest and most extensively studied in the New World (Estrada, 1965), developed for about 3000 years during the prehistoric *Formative period* (5000–1000 BC). Its relative internal chronology, (Hill, 1972–1974), is based on ceramic stylistic indicators, and consists of eight main cultural phases. It was validated by the stratigraphic position of the chronological indicators itself in deep archaeological sites like that of Real Alto, which was uninterruptedly occupied from phase I to VII. Valdivia potters produced 50 different vessel forms throughout the whole sequence, most of them being very good time-markers (Marcos, 1988).

An absolute chronology of Valdivia civilisation was based only on radiocarbon dates until 1990, when a joint project among the Universities of Guayaquil, Barcelona and Milano was supported by the EU (Martini et al., 1991).

TL dating was performed using *fine-grain* technique. The general TL characteristics of Valdivia sherds were particularly suitable for dating. They had high TL sensitivity and stability, linear behaviour versus artificial irradiation up to relatively high doses (30–40 Gy beta and 350–500 Gy alfa), absence of *spurious TL* (Martini et al., 1988) and of *anomalous fading* (Wintle, 1973). As a consequence, a very high precision in palaeodose evaluation could be obtained (4–5%). The uranium and thorium concentration in ceramic pastes and soils was relatively low (about 1/3 that of European mean values), while  $K_2O$  concentrations were in the usual range (1–2%). The per cent <sup>40</sup>K contribution to the annual dose-rate was consequently relatively high (40–60%). The maximum water uptake of samples (saturation water) was low (less than 6%), due to their very low porosity. External dose-rates were measured by in situ dosimetry (Martini et al., 1983), and a high homogeneity of the external radiation field was observed. As a consequence of the sum of all these favourable conditions, the errors in dose-rate evaluation were particularly low and the derived errors in the calculated ages are consequently limited to 5%, something seldom achievable.

TL dating results are reported in Table 1, where precision and overall error, calculated according to Aitken, 1985, are quoted for each phase. The two independent absolute chronologies (TL and <sup>14</sup>C) are compared in Fig. 1.

The chronology based on ceramics and ceramic technology (shape, decoration, and surface finish) was

#### Table 1

TL and radiocarbon dating results. TL means and errors are calculated according to Aitken, 1985, and the two numbers quoted for each date represent the precision and the estimated overall error, respectively

Phase	TL results	Radiocarbon results
Valdivia I	3430 (+190; $\pm$ 280) BC	4730–3380 BC
Valdivia II	3020 (+150; $\pm$ 260) BC	3140–2900 BC
Valdivia III	2820 (+70; $\pm$ 280) BC	2910–2660 BC
Valdivia IV	2480 (+60; $\pm$ 250) BC	2600–2500 BC
Valdivia V	2280 (+50; $\pm$ 220) BC	About 2400 BC
Valdivia VI	2040 (+30; $\pm$ 200) BC	About 2000 BC
Valdivia VII	1850 (+60; $\pm$ 200) BC	About 2000 BC
Valdivia VIII	1620 (+100; $\pm$ 220) BC	2030–1810 BC



Fig. 1. Valdivia culture: comparison between TL and <sup>14</sup>C chronologies.

substantially confirmed. The two independent results are in good agreement, except for Valdivia I, VII and VIII. While TL data for Valdivia I are actually obtained from ceramics whose shape only appears during the final phase I (Valdivia Ib), the others suggest that they antedate the respective phases by a couple of centuries. TL results for the intermediate phases are also able to precise the <sup>14</sup>C series.

Beside ceramics, TL dating is also applicable in principle to all objects of archaeological interest which both contain dosimetric minerals and which have been submitted to heating at high temperature during manufacture. As such, the application of TL dating techniques to bronze artefacts ((Zimmermann et. al., 1974) is in some cases possible through the age determination of their clay-cores or the ceramic-like residuals of lost-wax casting operation. TL dating of bronzes is therefore indirect. The age is not obtained from the object itself, and caution is needed in the interpretation and presentation of results.

TL dating of bronze is quite a cumbersome task: sampling sometimes needs special devices such as an endoscopic probe. The clay-cores are not always preserved in appropriate conditions and they are often not suitable for dating because of their low content of good dosimetric minerals. Moreover, bronze objects have frequently been radiographed for scientific, conservation or restoration purposes, thus, adding a normally unknown or at least hardly assessable contribution to the absorbed dose. In addition, the external dose-rate evaluation can be complicated by the shielding effect of the metal and by lack of information on the history of the object.

Despite these difficulties, over the last ten years in our laboratory, clay-core dating has been successfully applied to about thirty bronze objects. Some of these are of international importance, such as the Lupa and the bronze collection of the Musei Capitolini, the Chimera d'Arezzo and the statue of St. Peter at the Vatican Basilica (Martini et al., 1994).



Fig. 2. Distribution of samples dated according to typology and cultural period.



Fig. 3. Error distributions of dating results.

Before concluding the section on dating applications, it is perhaps worth remembering that TL techniques date the act of last firing of the sample: in most cases this corresponds to the age of the structure to which the sample belongs, but we can also deal with older or younger samples. Two examples of this correspond respectively to specimens (especially bricks) taken from abandoned structures to build a new one (reuse), and to interventions made to adjust or modify an existing one (restoration). We have dealt with such *anomalous* results in about 20% of the cases investigated during the last ten years.

The finding of samples younger than expected can often deepen the knowledge of the historic or archaeological problem. Conversely, reused samples can usually give only a *post quem* dating element, which is often useless or redundant. This was not the case in our study of the Abbey of Pomposa, one of the most interesting examples of Romanesque architecture in Northern Italy. The innovative and exceptional decoration of its atrium, made with differently coloured carved bricks, posed unanswered questions about its history and production technologies. Thanks to recent restoration work, several samples from the inward facing side of those decorated bricks have become available for dating analysis. Their dimensions are very close to the Roman bricks made in Northern Italy up until the 2nd century AD. Quite surprisingly, TL dating results (Bevilacqua et al., 1999) spanned from the 6 to 9th century, none the samples being Roman or coeval to the atrium building (1008–1046 AD). The decorations appear therefore to have been made with reused Romanlike bricks, produced during the early Middle Age. This suggests that local hands were working in continuity with the past in a period in which local production was thought to be interrupted, and stimulates a new approach to the study of local industry and trades, which hitherto was only perhaps supposed but not proven.

Before concluding our report on TL dating in archaeology, we give a short statistic presentation of the about 1300 ceramic samples submitted to our laboratory for dating over the last ten years. Their distributions, in accord with sample typology and the cultural period are shown in Fig. 2, while in Fig. 3 are reported the distributions of the percent overall error for all the samples and for each sample typology considered. TL dating in architecture (i.e. buildings) appears to be more likely to give precision higher than excavated samples or clay-cores. This was expected from the above mentioned more favourable conditions, deriving from the availability of large amount of material to be dated and from environmental data more easily determined. We have shown, however, that in those cases for which accurate measurements of both TL and dosimetric data are carried out and large amount of samples are

available, as in the Valdivia project, archaeological TL dating can also give precision levels as good as 5%.

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