

LUMINESCENCE DATING AND CULTURAL HERITAGE

MARCO MARTINI & EMANUELA SIBILIA

CNR-INFN, INFN and Università degli Studi di Milano Bicocca

via R.Cozzi 53, 20125 Milano

Abstract

Crystalline inclusions present in ceramics act as thermoluminescent dosimeters of the dose due to the natural irradiation field. Because of this various ceramic material (pottery, bricks, cooked clays, clay-cores) can be dated by thermoluminescence (TL). A short review of the main possibilities of TL dating is given, with some examples that underline the advantages and limits of this method in archaeology.

KEYWORDS: THERMOLUMINESCENCE, CERAMIC MATERIALS, ABSOLUTE DATING TECHNIQUES

KULCSSZAVAK: TERMOLUMINESZCENCIA, KERÁMIA, ABSZOLÚT KORMEGHATÁROZÁS

The Thermoluminescence

Thermoluminescence (TL) is the emission of light observed during the heating of insulating or semiconductor materials, provided that they have been previously exposed to ionising radiation (McKeever 1985; Martini e Meinardi, 1997; Chen and McKeever, 1997)

This irradiation may take place in the laboratory or in a radiative environment. Another possibility, which is exploited in dating applications, is when a naturally occurring material is irradiated by the radiation field of its natural surrounding.

The exposure to radiation perturbs the initial stable configuration of the material and the heating allows the release of the accumulated energy.

The existence of thermoluminescence is linked to the internal ordered structure of insulators, and to the presence of imperfections in its lattice. The process can be described, in a simplified way, recurring to the energy band representation of insulators and assuming the presence of two kinds of imperfection in the crystal, as shown in **Fig. 1**.

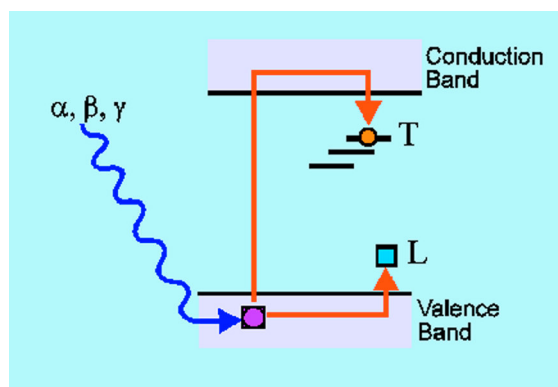


Figure 1. Traps levels in an insulating crystal

As a consequence of the exposure to ionising radiation, electrons and holes (vacancy of an electron) are produced in pairs: they can be captured in the electron and holes traps, whose energies are within the forbidden gap of the crystal. These traps are metastable, and usually their lifetime is very long at room temperature. The higher the exposure to ionising radiation, the higher the number of electrons and holes trapped. In general, linearity is observed between the two quantities.

When the temperature of the crystal is increased, the carriers are raised energetically and freed from their traps to the conduction band from which they can recombine with a trapped electron or hole, thus emitting TL.

The curve representing the intensity of emitted light as a function of temperature is called glow-curve, and its shape and intensity depend on the material and on the characteristics of the irradiation field, mainly the type and energy of radiation and its total amount (**Fig. 2**).

The study of the TL properties of a crystal is actually the study of the imperfections of its lattice,

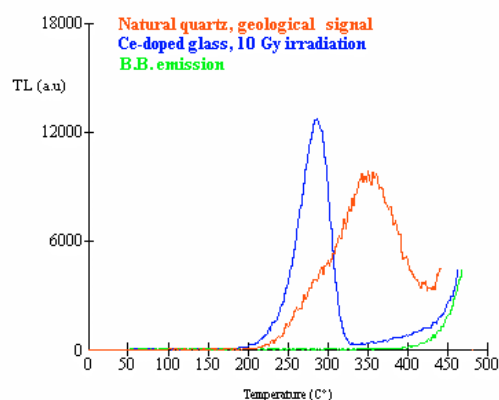


Figure 2. Examples of TL glow-curves

and TL is a very sensitive tool to detect imperfections even in very small quantities, and to understand the role played by defects and impurities in some physical properties of solids.

This last TL feature mentioned, i.e. its dependence on the amount of the energy absorbed during irradiation, called radiation dose, plays a primary role in the dosimetric applications of TL. (the SI unit for the energy absorbed due to the interaction of ionising radiation with matter is the gray (Gy).corresponding to 1 Joule/kg). In many cases, in fact, the intensity of the TL is directly proportional to the absorbed radiation dose. Once the dose response is tested using calibrated laboratory irradiations, any unknown dose producing a given TL signal can be determined. Several artificial and naturally occurring materials show this favourable property, covering a very wide range of dose (10^{-2} - 10^8 Gy approximately). They are widely used in radiation protection practices and can be used to measure the doses due to occupational exposure and those accrued as a consequence of nuclear accidents. New materials have been developed to best fit the characteristics required by the main specific applications which are personnel, environmental, medical, retrospective and high-dose dosimetry (McKeever et al., 1995).

Detection of TL signal

The definition of TL itself suggests a rather easy way to detect it: what is needed is in fact an apparatus which allows to heat the samples under controlled conditions, and an efficient light detection system. In most cases, the very low level of the emitted signal and the difficulties of controlling and measuring precisely the sample temperature require the use of complex and specifically designed systems. This is particularly true when TL intensity is very low, like in dating applications or when basic studies on defect centres are carried out.

In **Fig. 3** a schematic diagram of a TL measuring instrument is represented. Three main parts can be envisioned: the heating system, the detection system and the signal processing. The most common heating system is composed of a resistive planchet that heats up as a result of the passage of current through it. A common method of measuring the temperature is through the use of a thermocouple welded to the underside of the planchet. A photomultiplier tube (PMT) is normally used to detect the emitted TL.

In fact the efficiency of high-gain, very sensitive PMTs allow the detection of very low level signals with a convenient signal-to-noise ratio.

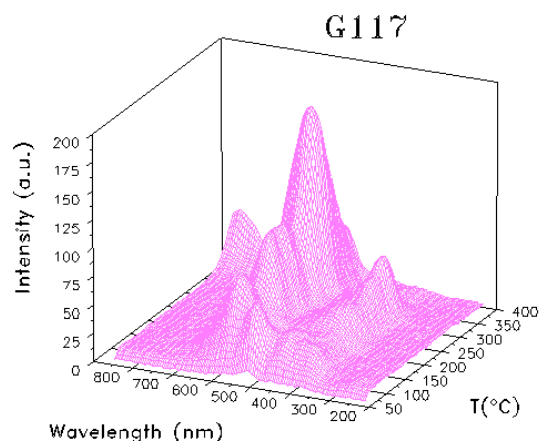


Figure 3.

Ancient mosaic glass. Wavelength resolved TL spectrum

The recent development of high sensitivity light detectors, such as intensified diode arrays and Charge Coupled Devices (CCD), has allowed the measurement not only of the amount of emitted light, but also of its wavelength (Martini et al., 1996), obtaining information about the centres involved in the recombination processes. An example of such spectrum is reported in **Fig. 4**.

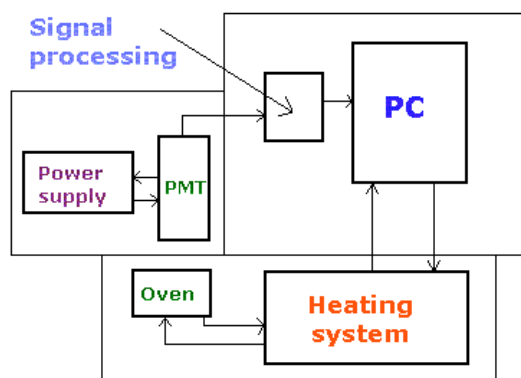


Figure 4.

Diagram of a typical TL measuring system

Thermoluminescence dating

Thermoluminescence dating is the only physical technique for determining the age of pottery presently available. It is an absolute dating method, and does not depend on comparison with similar objects. The application of thermoluminescence in archaeological and geological dating (Aitken 1985, 1990) is based on dosimetry: it stands on the fact that many naturally occurring TL mineral constituents of ceramics, including quartz and most

feldspars, are able to act as dosimeters for the amount of ionising radiation they are exposed to. This radiation mainly comes from the radioactive decay of uranium, thorium and potassium present in the ceramics itself and in its surrounding (typically the burial soil), at concentrations of a few parts per million. The radioactive materials having long half lives of 10^9 years or more, the radiation flux is practically constant.

An important point to single out is that, when pottery is fired, it loses all its previously acquired TL. Thus, after cooling, the natural radioactivity causes thermoluminescence to build up again so the older an object is the more light is produced (**Fig. 5**). The TL level measured in pottery is associated with the dose accumulated since it was fired in kiln, unless there was a subsequent re-heating. Any heating at high temperature acts as a *clock resetting* event. This usually occurs when the items are heated over 400°C . In archaeology, thermoluminescence dating is specific for ceramics bricks, cooking hearths, incidentally or deliberately fired rocks such as flints or cherts.

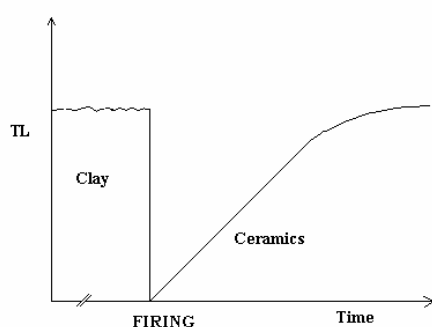


Figure 5. TL growth vs. time

If the radioactivity of the pottery itself, and its surroundings, is measured, the dose rate, or annual increment of absorbed dose, may be computed.

The age of the pottery, in principle, may then be determined by the relation

$$\text{Age} = \text{Absorbed dose} / \text{Annual Dose-rate}$$

Typically we are dealing with absorbed doses ranging from a few to a few tens of Gy. The dose-rate is usually within the range 1-10 mGy/year.

Even if the principles on which TL Dating is based are rather simple, the practical procedures are not. The precise evaluation of both absorbed dose and dose-rate requires the consideration of various factors affecting the calculations. For example, one of these is the way in which the different types of radiation, α , β , or γ , are absorbed by the thermoluminescent minerals contained as small crystals in the pottery. The amount of water

contained in pottery, changing its density, also influences the absorption of energy.

The main dating techniques were developed on the basis of the differences in absorbing radiation by grains of different sizes. The so called "inclusion" technique (Fleming, 1970) considers only quartz crystal grains in the range 100-200 μm extracted from the ceramic.

The second major TL technique is the "fine grain" (Zimmermann, 1971) which uses all the material that can be extracted, for instance by drilling the sample. A grain size separation is then operated by settling the obtained powder in acetone suspension. It is possible to select a grain size range, typically between 1 and 8 μm .

It must be mentioned that some complicating factors can occur, due to the specificity of the materials. In fact, while in dosimetry one can choose the best dosimeter available for a given radiation, in TL dating only the naturally occurring minerals can be used. The clay minerals have usually low TL; a few of them are hardly thermoluminescent at all; some may not have a straight-line relationship between dose and TL. In addition, some of the accumulated signal may be lost due to thermal and anomalous fading (Wintle, 1973), where part of the TL is lost without thermal excitation, or it may exhibit a spurious, non radiation induced component (Martini et al., 1988). Also, if the sample was poorly fired in antiquity, the TL clock would not have correctly set to zero.

The presence of one or more of these effects has great influence on the uncertainty of the final result. If they are absent or small, or can be compensated or corrected for, then the error limits on the dates obtained typically range from 4 to 8% of the age ($\pm 1\sigma$)

Dating applications

TL might in principle be used to date any archaeological material containing thermoluminescent mineral and subjected in the past to an heating sufficient to erase any previous signal. Ceramics, due to its widespread occurrence in archaeological excavations, is the more frequent material submitted, together with bricks from historical buildings.

The clay cores from lost wax metal castings may also be tested. Heated stone material, such as hearths, pot boilers, and burnt flints, can be dated as well, even if some regions are known to present problems for TL, like Indonesia and West Mexico: objects from these areas usually do not successfully yield TL dates, due to the very poor TL characteristics of the raw materials locally used.



Figure 6.
Bet Gemal excavation site

Possible applications of TL dating beyond man-made artefacts are in geology where aeolian, fluvial, coastal and, in some cases, marine sediments can be dated. In these cases the signal resetting is due to the exposure of sunlight during deposition. Also volcanic formations could be dated.

A few examples of application of TL dating techniques in various archaeological fields are reported in detail in the next section.

Excavation archaeology

An interesting example in excavation archaeology is the case of Bet Gemal (Strus, 2003), an Israeli village inhabited from II century BC to the Islamic period (IX century AD).

The site displayed exceptionally well preserved remains: a Roman-Jewish quarter, a Christian Byzantine settlement with several plants for oil and wine production (**Fig. 6**) and an Islamic dwelling place. Each group of remains is related to different chronological periods. The long occupancy of the site and the cultural and religious changes that took place resulted in a complex, cumbersome stratigraphy posing problems of absolute chronology, in particular regarding the duration of the different occupations. TL dating was performed on several domestic ceramics characteristic of the three periods. Supported by our results an absolute chronology of the site could be proposed. The Jewish occupancy had its break at the end of the I century AD, in the historic context of the Jewish-Roman Wars. For the two following centuries, the site should have been almost abandoned until the III century, when the repopulation of the site started and its prosperity grew; the remains of

workshops of ceramics, wine and oil presses testify the economical prosperity of this phase.

A successive development of the village occurred in the Byzantine period, linked to new constructions like a church and a further oil press that was functioning during the VI century. The last transformation of the village occurred during the VII century, after a destruction on a large scale probably due to the invasion of the Persian army in 614 AD or to the local Muslim victory over Byzantines in 643 AD. The destruction was followed by a general restoration of life, marked by the re-building of several houses and by new industrial and housing projects, until the final abandonment of the village somewhere in the IX century.

The impressive stone structure depicted in **Fig. 6**, the bigger of the three oil presses associated to the Byzantine phase, well testifies the economical importance of the site at that time.

Another relevant application is the study of the chronology of the Cham civilisation, that developed in central and southern Vietnam from 6th to 16th century.

In the frame of an Italian-Vietnamese Program of Cooperation an extensive TL dating project of the MySon religious complex started in 2005. The site shows the remains of more than 70 buildings of different styles (**Fig. 7**) built in different periods but always with the same building technique.

About 300 bricks and ceramics have been sampled and the presently available results show evidence of a chronology much more complex than supposed by former scholars, especially for what concerns the important edification phases occurred during X and XI centuries.



Figure 7.

A ruined tower at the MySon religious complex

Historical buildings

Since the stratigraphic techniques initially developed for archaeology have been extended to architecture, the relative internal sequence of the various building phases of a monument can be usually precisely determined. Their absolute chronology is however sometimes problematic or controversial. In such cases, the contribution of the

TL dating techniques could be conclusive (Galli et al., 2002).

It must be reminded, however, that care has to be taken when associating the TL age of a brick to that of the structure it belongs to, because the event that is determined is the last firing of the sample. Voluntary human actions (rebuilding, transformation, decay and restoration) can modify the position of a brick in the stratigraphic sequence of a building. Moreover, in case of reuse of materials from pre-existing structures, dates are older than the building; in case of upkeep or mimetic restoration, dates are younger than the building. In case of fire, this event will be dated.

The contribution of the archaeometric techniques to the study of ancient buildings is anyway very important. The main advantages of this kind of application are the availability of large quantities of material, the homogeneity of environmental radioactivity and the lesser extent of humidity fluctuation.

TL dating in architecture should therefore give uncertainty lower than in excavation archaeology, as confirmed by the statistical analysis performed on about 1300 ceramic samples submitted to our Laboratory for dating over the last ten years (Martini et al., 2001). It could be appreciated that errors lower than 6% are much more frequent when dating buildings rather than excavated samples.

As an example, we report the results recently obtained for the San Lorenzo Church in Milano (**Fig. 8**)



Figure 8.

Back view of S Lorenzo Church in Milano

The cathedral of S. Lorenzo in Milano, the more ancient testimony of roman and palaeochristian architecture in Milan, is a complex architectural structure that shows evident traces of several building interventions often lacking of sure chronological attribution. After performing a detailed stratigraphic analysis on both external and internal surfaces to fix the general building sequences, the different phases were dated with thermoluminescence and radiocarbon.

TL was applied only to unbroken bricks and fictile tubes sampled in several wall structures of the complex. Radiocarbon was used on wooden charcoal scrapes contained in the joint of mortars of walls. In absence of scrapes, calcium carbonate clots found in the mortars themselves were employed. In total, more than two hundred samples were analysed.

The very good agreement of all the results relative to the original phase allowed to indicate the narrow period 390-410 A.D. for the foundation of the tetraconch. It seems to be a more reliable estimation than the previous one based on historical ground. Later medieval reconstruction phases have also been uncovered.

Burnt flints

The possibility of dating burnt flints by TL appeared soon a great challenge to contribute in studying sites whose age is beyond the upper limit of radiocarbon dating (about 40.000 years), and when organic materials are not abundant or not well preserved. Flint is dense siliceous sedimentary rock whose basic component is SiO_2 , occurring as silica, cristobalite/tridymite and α -quartz.



Figure 9. Archaeological flints

Due to its hardness and conchoidal fracturing properties, it was largely employed in prehistory to manufacture a large number of artefacts (**Fig. 9**). Some of them were accidentally or deliberately heated and the burning is obviously essential for the erasure of the geologically accrued TL.

Goksu and co-workers (Goksu et al., 1974) highlighted the possibility of dating burnt flint, presenting at the same time the limits and the specific problems related to such materials: generally low TL sensitivity and sensitivity changes, spurious and regenerated TL and very low concentrations of radioactive elements, circumstance that attaches great importance to a precise evaluation of the ambient dose-rate. Despite the problems encountered in this application, flint dating is widely used and the results played, for instance, a primary role in the revision of the chronology of the presence of Neanderthal man and of modern human in the Middle-East.

We recently studied a group of 20 burnt flints from the prehistoric site of Fumane, in North Italy, Verona province (Martini et al., 2001). It is a huge cave, used as a shelter by ancient men, characterised by paleosurfaces extremely rich in bones and lithic objects. The study of this site is considered very important for the passage from Middle to Upper Palaeolithic and from Mousterian to Aurignacian age in Northern Italy and Europe. Some stratigraphic sequences of the site have been dated with radiocarbon but very few data regarding the human presence are available.

The chronology obtained by TL, spanning from 79 ± 11 ka to 57 ± 12 ka BP, added key information to the archaeological and palaeoenvironmental history of this Pleistocene period, up to now poorly dated.

Archaeological glasses

The chemical-physical behaviour of silica glasses suggested the use of TL techniques as a suitable method to date these materials. Actually, because of the amorphous nature of glass, numerous factors reduce its thermoluminescence sensitivity. The main problems encountered in glass dating are generally low TL sensitivity (TL emission per unit of dose) and the emptying of TL traps due to sunlight exposure or to the low stability of TL traps at room temperature. Both effects result in a loss of TL signal. Moreover, changes in TL sensitivity often occur after repeated heating and irradiation of the same sample. Due to these difficulties, at the present state of the art only a few percent of the samples analysed could be dated.

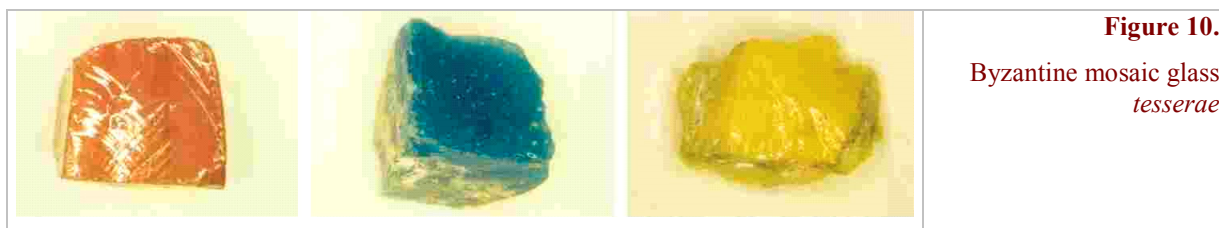


Figure 10.
Byzantine mosaic glass
tesserae

We focused our attention to a particular class of glass, the vitreous *tesserae* composing mosaics (Fig. 10). Our study was performed on samples chosen as representative of six sets of differently coloured glass mosaic tesserae. They all belong to wall mosaic decorations and were found in archaeological excavations or taken from mosaics to be restored, all well dated on archaeological grounds.

The thermoluminescent emission of these vitreous materials, lacking a long range periodic structure, is due to the impurities present or added to the glass network (Al, Mn, Cr...), the colour centres acting as electron traps and recombination centres. In fact, a good natural TL emission was observed in almost all tesserae, the blue ones being generally characterised by higher sensitivity.

Samples were submitted to different protocols for TL measurements, previously described (Chiavari et al., 2001) and their TL properties were investigated. This allowed selecting eight tesserae characterised by suitable TL behaviour (high sensitivity, trap stability, low optical bleaching and limited changes in sensitivity after heating), that were submitted to dating. They presented a TL sensitivity comparable with that of ceramics materials.

For the external annual dose-rates, mean values typical of the different provenance areas have been assumed, with errors taking into account possible wide variations. These assumptions determined errors quite high (15-18% of the age). It is however noticeable that the TL dates are generally consistent with the archaeological ones. It is also remarkable that we could date eight tesserae over the nineteen analysed: the percentage of suitable samples was about 40 % against the 5% reported for glasses up to now (Chiavari et al., 2000).

Clay-cores

The first application of TL techniques to clay-cores dates back to 1974, when D.W. Zimmermann (Zimmermann et al., 1974) succeeded in testing the authenticity of core materials from a Bronze Horse of the New York Metropolitan Museum of Art. Further attempts devoted to dating, soon

enlightened a series of difficulties, complications and limiting factors.

First of all, the application is in principle possible only for the objects cast by lost-wax technique, using the remains of thermoluminescent clay-cores heated contemporarily to the casting itself. The possibility of dating such materials depends on its mineralogical composition, and particularly on the abundance of “good” thermoluminescent minerals like quartz and feldspars. A high concentration of carbonates and/or organic material is generally a disadvantage, for the associated spurious, not dose-dependent TL emission. Another phenomenon that is observed with higher frequency than in ceramics is the anomalous fading, a process which empties deep traps at room temperature. The evaluation of the environmental contribution to the annual dose-rate can be problematic, both for the often unknown “archaeological history” of the object to date and for the need to evaluate the shielding effect of the bronze layer on the external irradiation.

Due to the sum of these circumstances, the achievable precision in dating bronzes is generally lower than in ceramics, the mean error being generally about $\pm 10\%$ of the age.

As a further remark, it must be pointed out that dating the clay core is not dating the bronze statue itself, except when the correlation between the ages of the two objects is sure, or highly probable. It must be reminded that any TL dating refers to the last heating at high temperature experienced by the item to date: in case of restoration or repair performed by heating, this last event will be dated instead of the original one (Martini and Sibilia, 2003).

The possibility of dating clay-cores is furthermore precluded if the object has been intensively radiographed before sampling out the core material. In such a case, unfortunately frequently recurring, the high energy X-ray exposure results in an accrued radiation dose that produces an additional TL emission, superimposed on the archaeological one. The evaluated palaeodose is consequently meaningless.

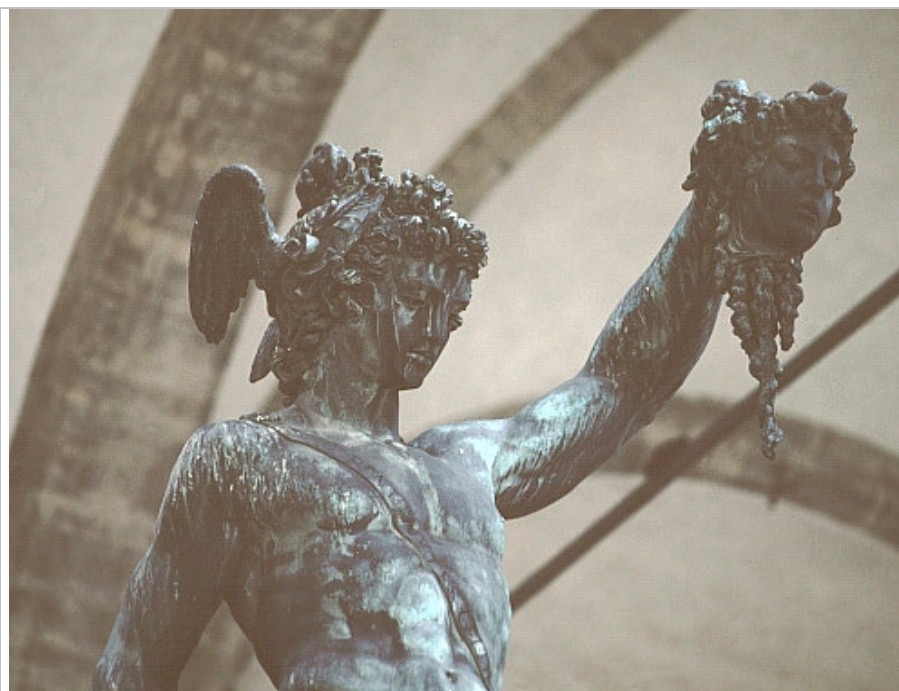


Figure 11.
Benvenuto Cellini, Perseo

Nevertheless, things are not always so discouraging, and often very satisfactory results can be obtained, like in the case of the Cellini's Perseo (**Fig. 11**) Benvenuto Cellini (Florence, 1500-1571) wrote that a "great cry of admiration" arose from the throng gathered to watch the unavailing of his *Perseo* in the Loggia dei Lanzi on April 27th, 1554. After about five hundred years of open air exposure, the state of conservation of the statue was critical, due to the polluted, aggressive urban atmosphere, transforming its historical patina from insoluble to soluble salts. It was therefore fully restored and its disassembling gave access to its interior, where important fragments of clay-core were found. In this case, TL dating was mainly performed to check the reliability of the technique, being the dating itself beyond dispute.

The dating result, 1540±35 AD, is in very good agreement with the historical records, confirming the potential of such application, the reliability of the laboratory protocols and the accuracy and precision of instrumental calibrations.

Conclusions

TL dating of ceramic materials is nowadays a consolidated and powerful technique which supports the archaeological and archaeometric researches.

Precision as good as ±5% in the evaluation of the age of various kinds of archaeological findings are often reached, allowing the solution of archaeological or historical problems arising from samples chronologically relatively close.

A systematic comparison of TL dating results with those obtained by other absolute dating techniques like radiocarbon and dendrochronology and the dating of samples already well independently dated on archaeological or historical grounds is highly recommended, in order to check and improve precision and accuracy of the laboratory experimental procedures.

References

- AITKEN, M.J. (1985): Thermoluminescence Dating, Academic Press, New York, 359 pp.
- AITKEN M. J.(1990): Science-based Dating in Archaeology, Longman, London, 274 pp.
- CHEN R. & MCKEEVER S.W.S (1997): Theory of Thermoluminescence and Related Phenomena, World Scientific, Singapore, New Jersey, London, Hong Kong, 559 pp.
- CHIAVARI C., GALLI A., MARTINI M. & SIBILIA E. (2000): Archaeometric considerations regarding ancient mosaic glass tesserae. *Rivista della Stazione Sperimentale del Vetro* **6**: 130-134.
- CHIAVARI C., MARTINI., SIBILIA E.& VANDINI M. (2001): Thermoluminescence characterisation and dating feasibility of ancient glass mosaic, *Quaternary Science Reviews* **20**: 967-972.
- FIENI L., GALLI A., MARTINI M., MONTANARI C. & SIBILIA E. (2004): Thermoluminescence and ¹⁴C dating of brick structures in S. Lorenzo church in Milano. Late

Antique and Medieval phases. *Proceedings of the 34th Int. Symposium of Archaeometry*, Zaragoza, 3-7 May 2004: 55-60.

FLEMING S.J. (1970): Thermoluminescent dating: refinement of the quartz inclusion method *Archaeometry* **12**: 133-147.

GALLI A., MARTINI M., MONTANARI C. & SIBILIA E. (2002): Thermoluminescence (TL) dating of historical buildings: an intriguing technique for the history of architecture *Proceedings of the 33rd International Symposium Archaeometry* Amsterdam, 22 -26 April 2002: 428-431.

GOKSU H.Y., FREMLIN J.H., IRWIN H.T. & FRYXELL R. (1974): Age determination of burned flint by a thermoluminescent dosimetry phosphors. *Science* **183**: 651-654.

MARTINI M. & MEINARDI F. (1997): Thermally stimulated luminescence: new perspectives in the study of defects in solids. *La Rivista del Nuovo Cimento* **20-4(8)**:1-71.

MARTINI M., PARAVISI S. & LIGUORI C. (1996): A new high sensitivity spectrometer for 3D-thermoluminescence analysis. *Radiation Protection Dosimetry* **66(4)**: 47-51.

MARTINI M., SIBILIA E. (2003): Dating the cast of bronze statues by thermoluminescence *Proceedings of the International Conference Archaeometallurgy in Europe*, Milano, 24-27 September 2003, **2**: 331- 336.

MARTINI M., SIBILIA E. & FERRARO L. (2001): A new data base of TL dates, *Proceedings of the 3rd International Conference on Science and*

Technology for the Safeguard of Cultural Heritage in the Mediterranean Basin, Alcalà de Henares, 9-14 July 2001: 387-390.

MARTINI M., SIBILIA E., CALDERON T. & DI RENZO F (1988): Spurious TL in archaeological ceramics: a study of affecting factors *Nuclear Tracks* **14**: 339-345.

MARTINI M., SIBILIA E., CROCI S. & CREMASCHI M. (2001): Thermoluminescence (TL) dating of burnt flints: problems, perspectives and some examples of application *Journal of Cultural Heritage* **3**: 179-190.

MCKEEVER S. W. S. (1985): Thermoluminescence of solids, Cambridge University Press, Cambridge, 390 pp.

MCKEEVER S.W.S., MOSCOVITCH M. & TOWNSEND P.D. (1995): Thermoluminescence Dosimetry Materials: Properties and Uses, Nuclear Technology Publishing, Ashford, 221 pp.

STRUS A., Khirbet Fattir-Bet Gemal. Two Ancient Jewish and Christian Sites in Israel, LAS, Roma, 552 pp.

WINTLE A.G. (1973): Anomalous fading of thermoluminescence in mineral samples. *Nature* **245**: 143-145.

ZIMMERMANN D.W. (1971): Thermoluminescent dating using fine grains from pottery. *Archaeometry* **13**: 29-52.

ZIMMERMANN D.W., YUHAS S M.P & MEYERS P. (1974): Thermoluminescence authenticity measurements on core materials from the Bronze Horse of the New York Metropolitan Museum of Art. *Archaeometry* **16(1)**: 19-30.