LUMINESCENCE DATING OF THE TANAGRA TERRACOTTAS OF THE LOUVRE COLLECTIONS

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Abstract: In connection with the exhibition *Tanagra - Myth and Archaeology* (Paris, 2003; Montreal, 2004), we investigated the authenticity of some 140 terracottas from the Louvre collections by luminescence dating (thermoluminescence and optically stimulated luminescence). For these terracottas being pieces from a collection, only the dose due to internal radioactivity could be derived from the direct measurement of the internal concentration of radioelements. To estimate the contribution of the external environment, we had to reconstruct the moisture content and the gamma dose rate. The moisture content was based on some indications about the site found in 19th century literature. We reconstructed the external dose rate received by the Tanagras from the ratio of the measured palaeodose to 2300 years. This result agrees well with a low radioactive soil known to be characteristic of the mainland Greece.

Applying such values of the external dose rate to our Tanagra, we obtained an age distribution showing two maximums, one at 2300 ± 400 years, the other at 150 ± 50 years.

1. INTRODUCTION

At the end of the 1860's, the inhabitants of Vratsi in Beoatia (Greece) working in their fields excavated ancient tombs corresponding to the necropolis of the antique city of Tanagra. The ages of the tombs covered a large chronological range from the Geometric (9th century BC) to the Hellenistic (3rd-1st century BC) period (Rayet, 1875). Small terracotta figurines were found in great numbers inside and outside the tombs of the the Hellenistic period.

The aspect of the Hellenistic figurines met the taste of 19th century middle-class for the reality of the life in the Greek antiquity, as opposed to Gods and Goddesses more appreciated by earlier aristocratic collectors. Within a few years, Tanagra had become a generic term to name a draped young lady. Actually Tanagra figurines not only represent women, a large part of figurines show young boys and actors. In addition, the so-called Tanagras do not come only from Tanagra and its surroundings (Beoatia and Attike). Tanagra-like small figurines were created all over the Mediterranean area (Myrna, Alexandria, Tarent). The Tanagra and Tanagra-like market quickly became a place of speculation (Belle, 1876). In 1872, the Louvre museum bought one hundred statuettes (Rayet, 1875), followed by other great institutions like the British Museum and by private collectors.

This led to the production of fakes. As most of the figurines came from illegal diggings made by peasants far from the eyes of the antiquity merchants, it was easy to produce fakes to cover the large demand (Rayet, 1875). Three main types of fakes exist. First, the pure inventions of the 19th century, made by contemporary artists, were figurines with a style distinct from the antique figurines, with a mul tiplication of the folds and draping. Second, were Tanagras obtained by moulding; being proto-industrial products, several generations could be derived from the same prototype. It was then easy to create fakes based on the antique or modern mould. Between the fake and genuine are the pastiches where pieces from various genuine figurines are put together to create a modern piece.

Using thermoluminescence dating, Goedicke (1994) showed that some 20% of the Tanagra figurines in the Berlin collection are modern copies. Following the work in Berlin, some twenty-five pieces of the Louvre collection were investigated by thermoluminescence in the Research Laboratory of the French Museums between

1994 and 1997. When in 1998 an exhibition was planned at the Louvre in co-operation with the Montreal Museum of Fine Art, *Tanagra - Myth and Archaeology* (Paris - Montreal, 2003), a large investigation of some 200 figurines from the Louvre collections was decided. The set included only pieces from Beoatia (Thebes and Tanagra) and Attike (Athens). The aim of the investigation was to characterize the material, clay, and pigment, and to define criterions of authenticity. The present paper reports the result of the luminescence dating work (June 2002 – February 2003) with the aim to verify the authenticity of the figurines.

2. EXPERIMENTAL TECHNIQUES

Sample preparation

A statuette was sampled using a 1.8 mm diameter tungsten carbide drill. Some 200 mg of powder was collected: 100 mg for luminescence measurements and 100 mg for chemical analysis (ICP-MS / ICP-AES). The choice of the location of the sample on the statuette was made in agreement with the curators. For practical reasons, mainly due to the small size of the pieces, only 140 statuettes were sampled for luminescence dating. We had also to reject the statuettes studied by X-ray radiographies in the past (it was the case of the famous *Blue Lady*). It should be noted that some sampling was made in the plate supporting the figurine.

After etching in 10% HCl and washing in water, ethanol and acetone, the 4-13 mm fraction was selected by sedimentation into tubes filled with 8 cm height of acetone and deposited on 9.8 mm diameter stainless steel discs. All these operations with the exception of the HCl etching, are automated (Zink *et al.*, 2002). Sixteen discs were prepared for thermoluminescence and four for OSL.

Measurement apparatus

In the 90's, investigations were done by additive TL using a Daybreak 1100 reader. The luminescence was detected through a combination of 7-59 x BG39 filters by an EMI 9635QA photomultiplier. The heating was limited to 500°C followed by a prompt cooling. The external irradiations were carried out using a Daybreak 801 multi sample irradiator with a 3.7 GBq beta $^{90}Sr/^{90}Y$ source (3.82 Gy/min on 1/6/2002) and a 18.8 MBq alpha ^{238}Pu source (7.78 mm^{-2}/min on 1/6/2002).

For the set of measurements carried out in 2002-2003, the luminescence measurements were performed with a Risø TL/OSL DA-15 set fitted with a $^{90}Sr/^{90}Y$ source delivering 7.89 Gy/min (on 1/6/2002). All measurements were made using an EMI 9235QA photomultiplier.

We used a double single aliquot regenerated OSL (SAR-OSL) protocol. The irradiations were carried out using the internal $^{90}Sr/^{90}Y$ source. After each irradiation, the disc was preheated at a temperature T. For each sample we used four discs corresponding to four different temperatures (220°C, 270°C, 320°C and 370°C). The disc was first stimulated by an IR laser diode (830±10 nm; 50 % of 450 mW/cm^2 full power) at 60°C during 100s and then stimulated at 125°C for 100s by blue diodes arranged in 21 pairs (470± 30 nm; 50 % of 19 mW/cm^2 full power). The luminescence was detected through a 7.5 mm thick U-340 filter. To prevent the leakage of radiation and stimulation to adjacent positions, the discs were placed only on the odd positions. All measurements were recorded by integrating over one second per channel. To determine the alpha efficiency, the disc was irradiated by an alpha external source, and promptly measured by OSL in the same conditions as previously. After normalisation by a test dose, the response was compared to the beta growth curve.

For additive thermoluminescence, the discs were irradiated by the external beta and alpha sources. After irradiation, the discs were stored in darkness at 50°C during 1 to 3 months. After a preheat up to 220°C, the disc was directly cooled to 60°C and then heated up to 650°C and the remaining signal was annealed at 650°C during 2 minutes. The luminescence was detected through a combination of 7-59 x HA-3 Filters. To control fading, a test disc previously annealed at 650°C was irradiated and stored together with the other discs. After measurement, the test disc was irradiated again and promptly (around 4 minutes after irradiation) measured to have a reference.

Alpha counting was carried out with three Daybreak 582/583 alpha counters using a 12 mm diameter cell. X-rays analysis was carried out by energy dispersion spectrometry (EDS) using a scanning electronic microscope.

ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectrometry) and ICP-MS (Mass Spectrometry) were made at the Centre de Recherches Pétrographiques et Géochimiques in Nancy and analysed by A. Bouquillon at the laboratory (Bouquillon *et al.*, in print).

3. MEASUREMENTS RESULTS

Palaeodose

A first test using a SAR-TL protocol was not successful. It was due to a great change in sensitivity after the first measurements (in comparison with the natural signal), which could not be corrected by the test dose response. We attributed this to a modification of the self-absorption of the grains.

The full set of Tanagras was measured by single aliquot regenerated (SAR) OSL and some forty of them were investigated by additive thermoluminescence (TL). No measurable fading effect of the thermoluminescence was observed between one minute and 3 months for our samples. Although we employed a double-SAR OSL protocol, IR-OSL was extremely rare. When we began the study, the α-values were not measured for OSL and we used an average based on the α-value for TL. After a month, we added an easy method to determine this parameter in OSL by adding a cycle in the OSL-SAR protocol with alpha irradiation, measurement and then test dose and measurement. The intensity due to alpha dose was normalised by the test dose. The intensity thus calibrated was plotted on our growth curve. Hence, the beta dose equivalent to the alpha dose was graphically estimated. Later, the α-value was calculated in the same way as in TL. The results had a good precision, better than for TL (**Table 1**). Both α-values are known only for six samples, and it is difficult to discuss their differences. Obviously the average of the α-values are distinct for TL and OSL. It can correspond to a difference in the physical process. Generally the TL and OSL gave similar equivalent doses. We chose to concentrate our work on the OSL.

Annual dose

The estimation of the annual dose was more complicated. Being collection pieces, only the internal concentration in radioelements could be directly measured giving information on the contributions of alpha and beta dose rate. Nineteen Tanagras had been investigated by alpha counting and EDS in the 90's. In 2002, all the collection was investigated by ICP-AES (majors) and ICP-MS (traces) to determine the origin of the clays and identify the sites of production. In general, the various methods are in agreement. The only difference between ICP-MS and alpha counting comes from the [Th]/[U] ratio. For alpha counting, due to the small size of the sample holder (diameter 12 mm), it is not possible to use pair counting to determine the Thorium content (ca. 1- 10 pairs/week). Hence, we used an arbitrary value of 3.167. In fact, the elemental analysis showed a higher [Th]/[U] ratio close to 4.0. Only the concentrations obtained by elemental analysis were used in the age calculation.

Table 1. *Alpha efficiency (α-value) measured for OSL and TL. (Lab. No. – laboratory reference number; Inv. No. – Louvre reference number).*

Lab. No.	Inv. No.	α-value OSL	α-value TL
FZ29602	MNB589		0.210
FZ29985	MNB595		0.160
FZ30040	CA1627	0.041	
FZ30042	MNB1003		0.080
FZ30045	CA3005-2	0.063	0.080
FZ30049	MNB481		0.110
FZ30050	MNB551	0.055	
FZ30055	MNB573	0.097	
FZ30174	MNB585	0.102	0.120
FZ30286	MNB489	0.061	0.220
FZ30363	MNB493	0.051	
FZ30364	MNB497		
FZ30365	MNB560	0.091	
FZ30366	MNB577		0.060
FZ30459	MNB1008		0.090
FZ30463	MNB492		0.140
FZ30464	MNB494		0.200
FZ30467	MNB482		0.120
FZ30494	MNB559		0.080
FZ30539	CA2152	0.071	
FZ30543	CA2162	0.057	
FZ30588	CA2168	0.050	
FZ30589	CA3005-4	0.059	
FZ30590	CA3005-5	0.061	
FZ30591	MNB476	0.070	0.130
FZ30628	MNB596	0.077	0.140
FZ30712	CA588		0.020
FZ30713	CA2165	0.076	0.130
FZ30750	CA2552	0.061	
FZ30751	MNB447		0.160
FZ30753	MNC730		0.220
FZ30754	CA265		0.140
FZ31189	CA806	0.073	
FZ31254	MNC747b		0.120
	average	0.068	0.130
	st. dev.	0.016	0.053

Moisture

To estimate the contribution of the external environment, we must reconstruct the moisture content and the gamma dose rate. For practical reasons it was not possible to use a drying oven to measure the moisture inside the Tanagra. Moreover, the water content in the present location of conservation (gallery or storeroom) is not representative of the moisture in the buried conditions. It is necessary to choose an arbitrary value, the most representative to our knowledge about the average moisture percentage. For this purpose we used two indications. Following Aitken (1985), the porosity of ceramic varies in the range 5-25 %. The sampling showed that the earth was crumbly. As a result we assumed a high porosity, some 20-25 %. Moreover, the authors from the 19th century described the weakness of the pieces due to high moisture (Rayet, 1875). Therefore, we suggested a high level of moisture around 16% which corresponds to a fraction of porosity of 60-80 %.

Gamma dose rate

To reconstruct the external dose rate in a general case, we created a database containing more than 725 external dose rates reported in the literature with a worldwide distribution (Zink, 2002). More than 95 % of the values are below 2.0 mGy/a. The distribution of the values show two main maximums, the first around 0.4 mGy/a corresponding to low radioactive soils as loess or sediments, the other around 1.2 mGy/a attributed to high radioactive soils such as granites and basaltic rocks. An intermediary maximum around 0.8 mGy/a corresponds to mixed soils, e.g. fluvial deposits from various origins. Continental Greece is mainly constituted by weakly radioactive soils (Clouvas *et al.*, 2001). Hence we expect values close to the first maximum.

Usually, with an artifact of unknown origin (i.e. with an unknown external dose), we assume a local origin of the earth used for the terracotta, the so-called «local hypothesis». Hence, we take for the external gamma dose rate the same value as the internal gamma dose rate. In this case, considering the internal content in radioelements, we found a mean value of 0.62 ± 0.29 mGy/a (**Fig. 1**). And we assume an uncertainty of 0.6 mGy/a, corresponding to the standard deviation of a uniform distribution between 0 and 2mGy/a. With such uncertainty, higher than the simple distribution of the internal gamma dose rate, all chemical modifications during the manufacture of the piece can be neglected.

For the Tanagras, we used another method. We tried to reconstruct the dose rate experienced by the Tanagras. If the pieces are genuine, their age must be around 2300±100 years. We can assume too, that they laid in only one place, except during the last century. Hence, averaging the palaeodose on 2300 years, we obtain for each Tanagra an annual dose rate. Using the internal dose rate and the fraction of moisture, it is possible to calculate a distribution of the external dose rate among the different statuettes (**Fig.1**). This distribution can be fitted by a Gaussian of an average of 0.55 mGy/a and a standard deviation of 0.20 mGy/a.

The two methods yielded similar results for the average external gamma dose rate corresponding to weakly radioactive soils. They gave us the mean ambient dose rate in Beoatia and Attike during the last 2400 years. But for individual Tanagra, the two methods did not always give similar results. When the differences were larger than the uncertainties, we assumed that the local hypothesis failed. The local hypothesis gave us the dose rate of the terracotta, and indirectly of the clays used to produce the piece. On the other hand, the reconstructed dose rate gave us a good estimation of the ambient dose rate, i.e. of the soil where the Tanagras were buried. The agreement between the two hypotheses implied from a radiometric point of view that the object was produced and then conserved in the same region. The rejection of this agreement led us to assume a difference between the place of production and the place of conservation (mainly tombs).

Such analysis could be helpful to identify trade routes between central Greece and volcanic regions like Great Greece or Cyclades. It is known that some Tanagra moulds travelled across the Mediterranean area.

4. DISCUSSION

For the calculation of the age we decided to take the value for the external dose-rate given by the reconstructed dose rate as 0.55±0.20 mGy/a, which appeared as the most representative of the external dose rate experienced by the Tanagras. We obtained an age distribution showing two maximums, one at 2300±400 years, the other at 150±50 years, corresponding to the age of genuine Tanagras and to the age of the 19th century copies (**Fig. 2**), respectively. Hence, we were able to separate the two groups. The fakes seem to have undergone similar annual palaeodosimetry as the genuine pieces. In the previous work on the dosimetry in the palaces and museums in Paris and surroundings, we observed a large range of dosimetry from 0.30 to 1.26 mGy/a (Castaing *et al.*, 2004). In particular, in the rooms of Greek, Etruscan and Roman Antiquity of the Louvre museum, the observed dose rates span between 0.43 and 1.02 mGy/a. It is difficult to reconstruct the exact dose rate received in the museum as the collections are moved from one room to another.

Our results showed that the same clay groups identified by chemical analysis were observable in the genuine pieces as well as in the fakes, showing that the same clays were used by modern forgers as in antiquity. No modern pigments were used, only the use of Egyptian blue (cuprorivaite) can conversely be of use as a criterion of antiquity. Luminescence dating appears then as the only laboratory method to identify fakes (Bouquillon *et al.*, 2003). After discussion with curators, our results agreed well with their observations. One problem concerned a figurine of an actor (MNB904). A similar figurine, now in the Hermitage Museum (St Petersburg) was actually

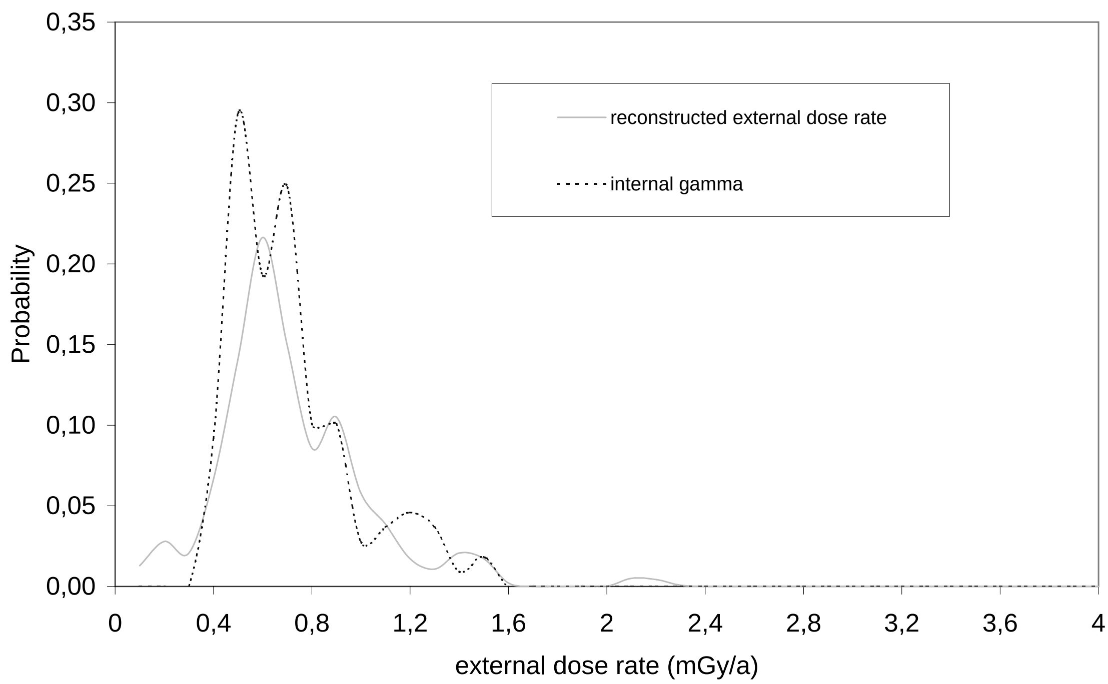

Fig. 1. *Probability density function of the gamma dose rate based on radioelement contents in the figurines (dashed line), compared with the probability of the reconstructed external dose rate (solid line). The reconstructed external dose rate (D'ext) was estimated for each Tanagra using the stylistic age (200 - 330 BC), the equivalent dose (De) and the internal dose rate (D'int) (D'ext=De/Age - D'int).*

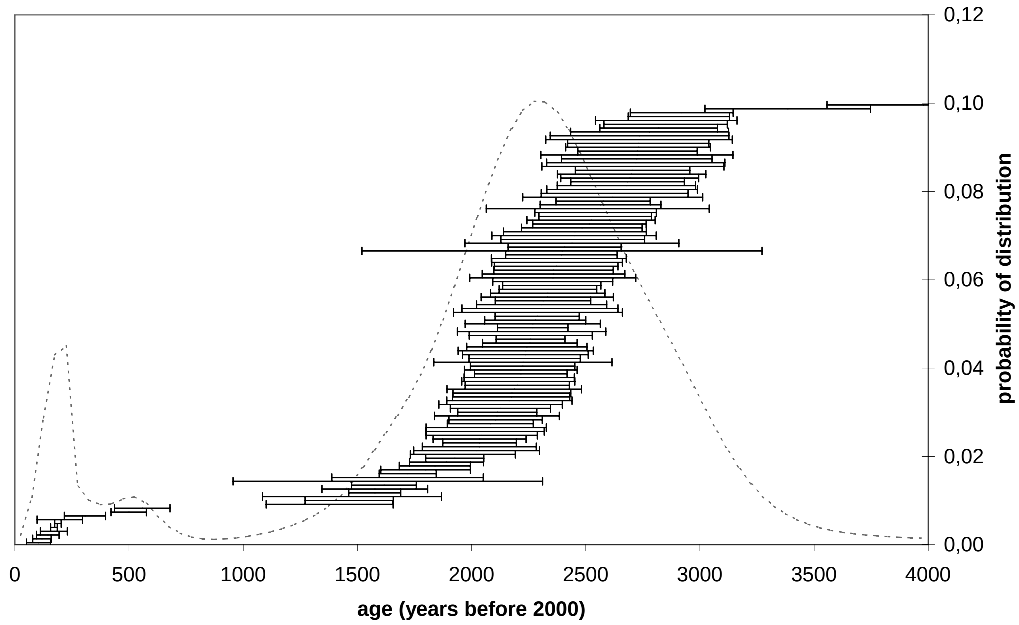

Fig. 2. *Probability density function of the age of our Tanagra set (dashed line), based on SAR-OSL measurements, taking 16% for moisture and 0.55±0.20 mGy/a for external gamma dose rate. The individual age (with 1s uncertainties) are plotted in increased order from bottom to top.*

found in a supervised digging which obviously indicated that this type is ancient. But after discussion, a new examination by the curators showed that the stylistic technique of the piece from the Louvre is in fact fully modern (Becq, 2003).

5. CONCLUSIONS

To be able to use luminescence dating for pieces from a collection, some hypotheses are needed. For the Tanagras, we have reconstructed the mean ambient dose rate in Beoatia and Attike regions. Our investigation showed that the percentage of fakes in the Louvre collection is small compared with other museums (Goedicke, 1994). The gap of one year between the purchase of first Tanagras by the Louvre (in 1872) and by Berlin (in 1873) could explain such a difference.

Compared to the simple typo-chronology based on stylistic characteristics, luminescence dating first appears to be less precise. Our results on the Tanagras yield a weighted mean age of 2220±195 years, while curators and art historians can split the Tanagra century (200 – 330 BC) in four or five periods. But the moulding techniques made easy the re-cycling of older models. Some popular figurines could have been produced over more than a century. An ancient mould, or a mould made from ancient pieces, can be used to create modern fakes. In this case, the stylistic definitions based on marble sculptures are not sufficient to ensure authenticity. Then with a lower precision, but a higher reliability, the luminescence dating is safer to date Tanagra figurines.

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REFERENCES

Aitken M.J., 1985: *Thermoluminescence Dating*, Academic Press, London: 359 pp.

Becq J., 2003: 236 - Acteur en papposilène parodiant une tragédienne. (Actor as Papposilene parodying a tragic actress). In: Jeammet V., ed., *Tanagra, Mythe et archéologie (Tanagra, Myth and Archaeology)*, RMN, Paris: 303 (in French).

Belle H., 1876: Voyage en Grece (Travel in Grece). In: Charton E., ed., *Le tour du monde: nouveau journal des voyages (Around the world: new journal of travels)*, Hachette, Paris 32: 54-55 (in French).

Bouquillon A., Colinart S., Porto E. and Zink A., 2003:, Authenticité, matières et couleurs. Etude en laboratoire des Tanagréennes du Louvre (Authenticity, maters and colors. Study in laboratory of the Tanagra-like terracotta of Louvre). In: Jeammet V., ed., *Tanagra, Mythe et archéologie (Tanagra, Myth and Archaeology)*, RMN, Paris: 298 –301 (in French).

Bouquillon A., Porto E. and Zink A., in print: Tanagra, beauté et mensonge; recherche en laboratoire (Tanagra, beauty and lie; research in laboratory). In: Jeammet V., ed., *De l'objet de collection à l'objet archéologique: statut et fonction des Tanagra (From collection's object to archaeological's object: statute and function of the Tanagras)*, Musée du Louvre éditions – Editions Picard, Paris (in French).

Castaing J., Girod M. and Zink A., 2004: Radiation background due to radioactivity in palaces and museums: influence on TL/OSL dating. *Journal of Cultural Heritage*: 393-397.

Clouvas A., Xanthos S. and Antonopoulos-Domis M., 2001: Extended survey of indoor and outdoor terrestrial gamma radiation in Greek urban area by in-situ gamma spectrometry with a portable Ge detector. *Radiation Protection Dosimetry* 94: 233-246.

Goedicke C., 1994: Echtheitsprüfung an Tanagrafiguren nach der Thermolumineszenzmethode (Authenticity of Tanagra figurines based on thermoluminescence methode). In: Kriseleit I., Zimmer G., Cordelia J., eds, *Bürgerwelten, hellenistische Tonfiguren und Nachschöpfungen in 19.Jh. (Middle-class worlds, hellenistic terracotta and recreation in 19th century)*, von Zabern, Mainz am Rhein: 77-81 (in German).

Paris – Montreal, 2003: *Tanagra: mythe et archéologie (Tanagra, Myth and Archaeology).* In: Violaine Jeammet, ed., Musée du Louvre, Paris, 15th September 2003- 5th January 2004, Musée des beaux-arts, Montréal, 5th February - 9th May 2004., Editions de la Réunion des Musées Nationaux: 336 pp. (in French).

Rayet O., 1875:, Les figurines de Tanagra au Louvre (Tanagra figurines of the Louvre). *Gazette des Beaux-Arts* 11: 297-314; 551-558 (in French).

Zink A.J.C., 2002: Bayesian approach applied to authenticity testing by luminescence *Archeologia e calcolatori* 13: 211-216.

Zink A., Querre G. and Porto E., 2002: Automation of the chemical preparation for luminescence dating. *LED2002, Book of Abstract*: 206.