



APPLICATION OF DIFFERENT PROTOCOLS AND AGE-MODELS IN OSL DATING OF EARTHEN MORTARS

LAURA PANZERI^{1,2}, MICHELA CANTÙ³, MARCO MARTINI^{1,2} and EMANUELA SIBILIA^{1,2}

¹Dipartimento di Scienza dei Materiali, Università degli studi di Milano-Bicocca, Via R. Cozzi 55, 20125 Milano, Italy

²INFN, Sezione di Milano-Bicocca, piazza della Scienza 3, 20126 Milano, Italy

³Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia, via Ferrata 1, 27100 Pavia, Italy

Received 20 February 2017

Accepted 19 June 2017

Abstract: In this study, OSL dating was applied to earthen mortars, consisting in a quartz-rich aggregate dispersed in silty-clayey matrix. The samples were taken from two independently dated structures in Cremona, Northern Italy (Palazzo Raimondi, 1495–1499 AD and Palazzo Soldi, 1770–1790 AD). The evaluation of the equivalent dose (D_e) was attempted with both the multigrain and the single grain protocols using the 150–250 μm quartz fraction.

The reliability and effectiveness of the various statistical methods in identifying the well-bleached samples were tested. The use of the multi-grain technique gave unreliable results, due to the high amount of poorly bleached grains. With the single-grain technique, more promising results were obtained: in particular, the un-log MAM3 and IEU models allowed an accurate evaluation of the mortar expected age in most cases, even if the precision is still relatively low.

Keywords: mortar dating, OSL, quartz, single grain.

1. INTRODUCTION

Dating a building or identifying the sequence of its constructive and destructive phases can give thorough information about the development of the building itself, relating it to its historical context. It also allows, in many cases, to deepen our knowledge of the evolution of the construction technologies. The possibility of dating materials whose age is highly correlated to that of the architectural structure itself is therefore desirable. Many dating methods specific for organic and inorganic materials can be applied in the field of construction dating, the main being radiocarbon and luminescence dating, *i.e.* Thermoluminescence (TL) and Optically Stimulated Luminescence (OSL). TL is a well-established method for abso-

lute dating of brickworks. Nevertheless, sometimes this technique is not able to solve the dating problems of architectural historians because it gives the time elapsed since the firing in kiln (or any comparable later heating). The frequent practice of reuse (Martini and Sibilìa, 2006) and the use of unfired natural materials, such as mud bricks or stones, can make TL dating practically useless (Goedicke, 2003). Differently from bricks, mortar is prepared shortly before use and is usually not recycled. For these reasons mortar dating is a promising tool for chronological studies in archaeology and history of architecture. Even radiocarbon could be applied to mortar, dating the carbon dioxide absorbed by the material structure from the atmosphere during the crystallization process (Heinemeier *et al.*, 1997; Konow and Lindroos, 1997; Ringbom, 1997). A number of experiments have been carried out to satisfactorily extract calcite from mortar and date it with AMS (Lubritto *et al.*, 2015; Lindroos *et al.*, 2014; Ringbom *et al.*, 2014; Pesce *et al.*, 2012; Hale *et al.*, 2003) but until now it has not become a

Corresponding author: L. Panzeri
e-mail: laura.panzeri@mater.unimib.it

routine method, due to the contamination of the anthropogenic calcite with the geogenic one.

Once excluded TL (the TL minerals found in mortars are not subject to any heating), OSL is the best candidate for mortar dating. The basic assumption of this technique is that the quartz used as aggregate is optically zeroed during the process of quarrying and mixing, exposing the grains to sunlight (Zacharias *et al.*, 2002; Goedicke, 2003). The age is obtained through the evaluation of the amount of radiation dose absorbed since the preparation as a consequence of the exposure to the natural radiation field:

$$\text{Age(a)} = \frac{\text{Total absorbed radiation dose (D}_e\text{)}}{\text{Annual absorbed dose}} \quad (1.1)$$

While OSL is a well consolidated method for dating sediments (Aitken, 1998) the applications to mortars are still few (Urbanová and Guibert, 2017; Urbanova *et al.*, 2015; Panzeri, 2013; Goedicke, 2011, 2003; Bøtter-Jensen and Murray, 2002; Zacharias *et al.*, 2002). The main problem of this application is the incomplete zeroing of the OSL signal after sunlight exposure. A partial or inhomogeneous bleaching of quartz grains can be due to the presence of quartz of different origin whose bleaching characteristics can highly vary, as well as to the short duration of the exposure to light during the manufacturing process, especially for what concern the mixing and working procedures at the construction site. Further problems arise when dating young buildings, due to an OSL signal close to the threshold of detection (Goedicke, 2011).

For mortar dating the use of the coarse grain fraction was suggested by Goedicke (Goedicke, 2003). In this application to fourteen independently dated mortar samples from Germany he found that the larger the grains, the higher the probability of being well bleached. The multi-grain technique, measuring the OSL signal of aliquots consisting in hundreds of quartz grains, gave acceptable values of absorbed dose only with well-bleached samples while it obviously overestimated it in poorly bleached grains. The single-grain procedure (Bøtter-Jensen and Murray, 2002; Murray and Roberts, 1997), based on the OSL signal of each single quartz grain, allows the identification of the best-bleached grains in a heterogeneously and/or incompletely bleached mixture. This technique is highly time-consuming because usually only less than a few percent of the grains give acceptable signals. The analysis of a huge number of grains is therefore required (Goedicke, 2011, 2003; Duller *et al.*, 2000). An appropriate statistic elaboration of the experimental data is then a crucial step and several different approaches have been proposed. They are: 1) the weighted mean, 2) the Central Age Model (CAM, Galbraith *et al.*, 1999), 3) the Minimum Age Model (MAM, Arnold *et al.*, 2009; Galbraith *et al.*, 1999), with slightly modified versions, 4) the Internal-External Consistency Criterion (IEU, Thomsen *et al.*, 2007 and 2003). Their common goal is the identifica-

tion of the best-bleached fraction in heterogeneously bleached samples, to achieve a reliable evaluation of the true average historical equivalent dose. It seems that the IEU model and the MAM give good results in case of differently bleached samples (Urbanova *et al.*, 2015; Medialdea *et al.*, 2014; Jain *et al.*, 2004).

Aim of this work is to explore the potential of OSL dating of earthen mortars, a particular kind of mortar consisting in quartz-rich aggregate dispersed in silty-clayey matrix, in the light of the results available on lime mortars.

Earthen architecture is widespread mainly in rural areas, with buildings made of rammed earth or mud bricks and mortars (Aubert *et al.*, 2015; Fratini *et al.*, 2011). Sometimes, earthen mortars are also used to bind high quality fired bricks in churches, private buildings and civic architecture. This construction technique is witnessed in Cremona (Northern Italy, Po valley; Cantù *et al.*, 2016; Fieni, 1999; Bonazzi and Fieni, 1995), where the earthen mortars object of this study were sampled from two buildings whose structures were well dated on historical ground. To test the dosimetric properties of the samples we used both the small aliquot multigrain and the single grain OSL protocols (Murray and Roberts, 1997). We also tested and compared the reliability of the main statistical methods used for data elaboration and for final D_e estimation (Eq. 1.1).

2. MATERIALS AND METHODS

Sampling and sample preparation

The earthen mortars analyzed in this study are briefly described in Table 1. They came from two buildings located in Cremona, a small town in the Po valley, Northern Italy: Palazzo Raimondi (PR), built between 1493 AD and 1496 AD and Palazzo Soldi (PS), one of the most important residences of the town until the 15th century. They are similar in size, typology and construction techniques and were chosen for the completeness of the diagnostic investigations, historical surveys and available building stratigraphy. Those aspects allowed identifying mortars belonging to precisely and accurately dated structures: the original construction phase for Palazzo Raimondi (1495 AD) and a late 18th century restoration phase at Palazzo Soldi. The mortar samples were collected without exposing the material to daylight by means of a darkened environment made with a textile and using a red lamp. They were sampled using a chisel and a hammer. First of all the surface layer of the mortar was removed and then the inner part was collected and put into a black plastic bag. The upper and lower bricks in contact with each mortar joint were sampled as well. The mortars were very similar, consisting in an angular to sub-angular, moderately to poorly sorted, coarse to fine grained quartz-rich aggregate dispersed in a silty-clayey matrix. The matrix (grain size < 63 μm) usually ranged between 5 and 10 wt%, seldom reaching 20 wt%, and

Table 1. List of the analyzed samples with weight and their yield in 150–250 μm quartz.

Sample	Building	Date	Age (years before 2015)	Structure	Total weight (g)	150-250 μm quartz fraction (g)
PR1C				Basement 1	20.3	4.1
PR1D				Basement 1	15.3	1.8
PR2C	Raimondi	1490–1500 AD	520	Basement 2	23.6	3.6
PR2D				Basement 2	14.1	1.6
PR3C				Basement 3	12.1	1.5
PR3D				Basement 3	26.7	2.0
PS1C				Ground floor	24.3	5.1
PS2C	Pallavicino Soldi	1770–1790 AD	230	First storey	19.4	3.3
PS3C				Ground floor 1	28.2	2.8
PS3D				Ground floor 1	13.8	1.4

was composed of predominant quartz and fresh and/or weathered phyllosilicates. Little amount of carbonates might be present in the fine fraction due to lime addition to the mortars, especially in post-17th century samples. The aggregate (grain size > 63 μm) ranged between 75 and 95 wt%, mainly composed of quartz grains (30–40%), metamorphic rock fragments (mica schist and quartz-rich rocks, 5–30%), feldspars (5–10%), phyllosilicates (5–15%), amphiboles (0–5%), carbonates (0–5%), brick fragments (0–5%) and rare lime lumps (Cantù *et al.*, 2015).

For OSL measurements, samples were chemically treated, separated and prepared according to the standard procedures (Preusser *et al.*, 2008; Mejdahl, 1985) to obtain the 150–250 μm size quartz fraction. **Table 1** also reports the samples weight and their yield in 150–250 μm quartz.

Multi-grain aliquots were prepared by fixing the quartz grains onto 10 mm diameter stainless steel disks with silicon oil (covered area: about 3 mm diameter, corresponding to roughly 300 grains). For the single-grain procedure, the quartz grains were mounted on special 10 mm diameter aluminium disks with a grid of 10×10 holes holding the individual crystals.

OSL measurements and statistic models

OSL measurements were carried out with a Risø TL/OSL DA-20 reader. Photons were detected by a bialkali photomultiplier tube (EMI 9235QB) coupled to a 7.5 mm Hoya U-340 band pass UV filter (280–380 nm). Artificial β irradiations were given using a ⁹⁰Sr-⁹⁰Y source delivering 0.13 ± 0.01 Gy/s.

OSL measurements were performed using the single-grain procedure. The small aliquot multi-grain procedure was applied if a minimum of 10 multi-grain aliquots could be prepared.

The multi-grain aliquots were stimulated by an array of blue LEDs (470 \pm 30 nm) with a constant stimulation power of 54 mW/cm² or with IR LEDs (830 \pm 10 nm) with a constant stimulation power of 360 mW/cm². The samples were stimulated at 125°C for 40 s. Single-grain measurements were performed using the single-grain

laser attachment of the Risø system. The stimulation source was a 10 mW Nd:YVO₄ solid-state diode-pumped laser emitting at 532 nm, which can be focused sequentially on each of the 100 grains mounted on the disk (Botter-Jensen *et al.*, 2003). Each grain was stimulated for 1 s at 125°C.

The OSL signal of multi-grain aliquots was obtained integrating the first 0.64 s and subtracting the background signal (mean of the OSL signal of the last 8 s). The OSL signal of single-grains was obtained integrating the first 0.2 s less the background (OSL signal of the 0.7–0.9 s range).

To evaluate the absorbed radiation dose, D_e (Eq. 1.1), the Single Aliquot Regenerative-dose (SAR) protocol was used (Wintle and Murray, 2006; Murray and Wintle, 2003 and 2000), applying from three to five regeneration doses. A zero dose point was given after the highest regeneration dose measurement cycle to check the recuperation of the signal, followed by the repetition of the first regeneration dose for the recycling test. The purity of quartz samples was tested by OSL post IR measurements (Duller, 2003). The pre-heat temperature was chosen by means of the pre-heat plateau test.

For each sample, many D_e have to be evaluated, in principle one for each multi-grain aliquot or one for each single-quartz grain. They were estimated using the Risø Analyst 4.31.7 software by interpolating the natural sensitivity-corrected signal onto the dose response curve. The uncertainties associated to such individual D_e were calculated from counting statistics, curve fitting and assuming an instrumental reproducibility error of 2.5%.

To get the best estimate of the true value of a sample's D_e , all the individual values were statistically elaborated using the software R and Luminescence 0.4.4 package (<http://CRAN.R-project.org/package=Luminescence>), applying the statistics briefly described below:

- Weighted mean, using the individual dose uncertainty as weight ($w=1/\sigma^2$).
- Central Age Model (CAM, Galbraith *et al.*, 1999). It assumes that the logs of individual D_e estimates are evaluated from a normal distribution with a standard deviation representing the over-dispersion of the data.

- Minimum Age Model (MAM, Galbraith *et al.*, 1999). It assumes that the sample is composed of two or more populations of grains with different bleaching, leading to a multimodal distribution of D_e . The D_e values result from a truncated log-normal distribution, where the lower truncation point corresponds to the average log value of the fully bleached grains (namely the minimum age). The developed versions of MAM (MAM3 and MAM4) differ for the number of parameters used in calculation. In this case MAM3 was used, because the data sets do not always warrant fitting the 4-parameter model. The application of the MAM requires the knowledge of the amount of data dispersion, usually described by the over-dispersion parameter (OD). It corresponds to the σ value of CAM (Galbraith *et al.*, 1999). The over-dispersion is due to both intrinsic and extrinsic factors. Among the first ones are counting statistics, instrument reproducibility, other OSL characteristics of the sample, such as quartz sensitivity, predominance of the fast or slow component, *etc.*, variation in the dose rates at the grain size scale (Urbanova *et al.*, 2015), variation of the dose-rate of the beta source at the level of the 100 holes grid of SG discs (Lapp *et al.*, 2012). The main extrinsic factor is the incomplete bleaching. The intrinsic OD is required as input value to obtain the minimum age.
- un-logged MAM (ul-MAM, Arnold *et al.*, 2009). This model is a modification of MAM, and is based on the assumption that D_e derives from a normal distribution. It was developed to analyse data sets with zero or negative D_e values. This situation happens especially in very young samples (< 350 years) and the model is applied to the actual D_e estimates and their absolute standard error, rather than to their logarithms and their relative errors.
- Internal-External Consistency Criterion (IEU, Thomsen *et al.*, 2007 and 2003). It allows the identification of the proportion of best-bleached grains, assuming that they correspond to the lowest normal-dose population. This model only applies to single-grain results.

3. RESULTS AND DISCUSSION

Annual dose rate measurements and evaluation of the expected D_e

To obtain the annual dose-rates of Eq. 1.1, the radioactivity of the samples and of the surrounding bricks was measured. These analyses were necessary to evaluate the *true* value of the D_e absorbed by the single samples, as described in the following. ^{238}U and ^{232}Th concentrations were derived from alpha counting of the crushed bulk mortars and adjacent bricks using ZnS (Ag) scintillator discs and assuming a Th/U concentration ratio equal to 3.16 (Aitken, 1985). Contribution due to ^{40}K content was obtained from the total concentration of K measured by

flame photometry. The saturation water content of both mortars and bricks ranged from 10 to 12%. Taking into account the wet climate of the area and the high humidity conditions at the sampling points, the $75 \pm 15\%$ of saturation was assumed for calculations. The attenuation of the beta particles in coarse grain quartz was taken into account (Bell, 1979). The gamma external contribution mainly derives from the radioactivity of a 30 cm diameter sphere centered at the sampling point (Aitken, 1985). Such contribution was evaluated from the radioactivity concentrations of the mortars themselves and of the surrounding bricks (Galli *et al.*, 2014). The contribution of each material to the annual dose-rate was evaluated applying the infinite matrix approximation, with updated conversion factors (Guérin *et al.*, 2011). The radiation-matter interactions are similar in bricks and mortars, since the effective atomic mass Z^* is similar in the two materials, and so do the mass attenuation coefficients (evaluated to approximately $3 \cdot 10^{-2} \text{cm}^2/\text{g}$ at 2.5 MeV). To model our system we considered a sequence of homogenous 50 mm thick bricks assembled with 10 mm-thick mortar layers, as obtained after *in situ* measurements. In these conditions the brick contribution to the external dose rate within the interaction sphere does not exceed 40%.

The main results of radioactivity measurements are reported in Table 2, together with the resulting dose-rates, including a 0.15 mGy/a cosmic ray contribution (Prescott and Hutton, 1994).

Because both the annual dose-rate and the age of the samples are known, their *true* D_e can be derived by the inverse formula of Eq. 1.1:

$$D_e \text{ (Gy)} = \text{Age (a)} \cdot \text{Dose rate (Gy/a)} \quad (3.1)$$

Such D_e are obtained by multiplying the data of column 4 of Table 1 by those of column 8 of Table 2. They are listed in Table 2, column 9. They have been taken as reference values to which compare the experimental results given by the different experimental protocols and/or statistic elaborations, and referred to, in the following, as expected D_e .

Multi grain technique D_e

The multi-grain protocol was used for the six mortars listed in Table 3, those for which more than ten quartz aliquots could be prepared. Individual D_e values were rejected if one of the following criteria was not satisfied: recycling ratio between 0.9 and 1.1, recuperation < 5%, IR test < 10%.

Eventually, the percentage of acceptable aliquots ranged from 40 to 70%, as shown in Table 3, also reporting the D_e results given by weighted mean, CAM, MAM and ul-MAM models. The same results are visualized in Fig. 1, grouped by model and normalized to the expected D_e .

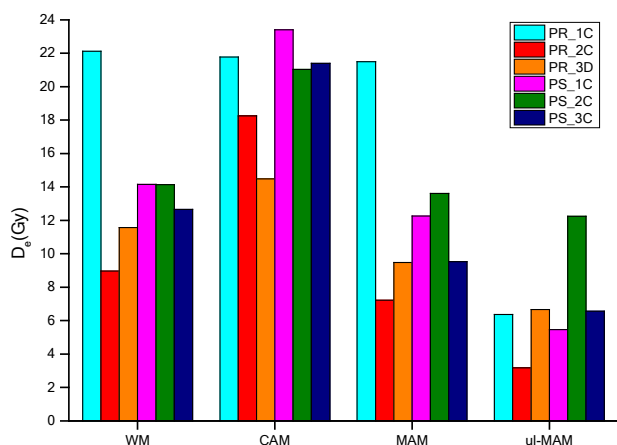
All the models overestimate the D_e , CAM giving the worse results. Regardless the statistic model used for data elaboration, the multi-grain protocol gives D_e values higher than expected, which will lead to a significant and

Table 2. Radioactivity concentration in mortars (column 2–4) and bricks (column 5–7), derived annual total dose rates and calculated expected D_e .

1	Mortars			Bricks			8	9
	2	3	4	5	6	7		
Sample	Th (ppm) $\pm 3\%$	U (ppm) $\pm 3\%$	^{40}K (ppm) $\pm 3\%$	Th (ppm) $\pm 3\%$	U (ppm) $\pm 3\%$	^{40}K (ppm) $\pm 3\%$	Annual dose rate (mGy/a)	Expected D_e (Gy)
PR_1C	8.90	2.82	1.21	8.99	2.85	0.89	2.18 ± 0.10	1.13
PR_1D	8.18	2.59	1.22	8.99	2.85	0.89	2.15 ± 0.11	1.11
PR_2C	9.70	3.07	1.33	9.96	3.15	1.23	2.43 ± 0.12	1.26
PR_2D	11.46	3.63	1.03	9.96	3.15	1.23	2.37 ± 0.15	1.23
PR_3C	8.53	2.70	1.04	9.79	3.10	0.78	2.10 ± 0.10	1.09
PR_3D	7.05	2.23	0.72	9.96	3.15	0.78	1.85 ± 0.09	0.96
PS_1C	9.81	3.10	0.83	8.99	2.85	0.83	2.27 ± 0.11	0.53
PS_2C	8.25	2.61	1.35	9.15	2.90	1.14	2.47 ± 0.11	0.58
PS_3C	9.46	2.99	1.37	9.96	3.15	1.14	2.74 ± 0.13	0.64
PS_3D	9.12	2.88	1.83	9.31	2.95	0.97	2.62 ± 0.13	0.62

Table 3. Multi-grain technique: Expected D_e and D_e evaluations with different statistical models.

1	2	3	4	5	6	7	8
Sample	Expected D_e (Gy)	# Measured Aliquots	# Accepted aliquots	D_e Weighted mean (Gy)	D_e CAM (Gy)	D_e MAM (Gy)	D_e ul-MAM (Gy)
PR_1C	1.13	11	4	25.0 ± 1.1	24.6 ± 1.6	24.3 ± 2.5	7.2 ± 1.5
PR_2C	1.26	31	21	11.3 ± 2.6	23.0 ± 2.8	9.1 ± 2.5	4.0 ± 1.2
PR_3D	0.96	37	24	11.1 ± 1.3	13.9 ± 1.1	9.1 ± 1.2	6.4 ± 0.6
PS_1C	0.53	31	19	7.5 ± 1.7	12.4 ± 1.6	6.5 ± 1.0	2.9 ± 0.7
PS_2C	0.58	30	15	8.2 ± 1.3	12.2 ± 1.2	7.9 ± 1.2	7.1 ± 0.4
PS_3C	0.64	32	23	8.1 ± 1.6	13.7 ± 1.6	6.1 ± 1.0	4.2 ± 0.8

**Fig. 1.** D_e obtained with multi-grain technique calculated with different statistical model and normalized to expected D_e .

systematic age overestimation. This is reasonably caused by an ineffective or inhomogeneous bleaching of the quartz grain. This can be due to the presence of hard to bleach grains and/or insufficient exposure to sunlight during the preparation of the mortar. Whatever the reason, the quartz grains did not receive enough sunlight to fully erase the luminescence signal acquired over geolog-

ical time and the bleaching process results in an incompletely and heterogeneously reset grain mixture. The multi grain technique is therefore unsuitable for this typology of samples.

Single-grain technique D_e

For the single-grain analysis, between 3200 and 4800 grains for each sample were measured. The percentage of grains giving a detectable OSL signal ranged between 15 and 25% (Table 4, 4th column). Even if relatively bright, the grains were rejected if one of the following conditions occurred: the signal was less than 3 standard deviations above the background, the recycling ratio was out of 0.75–1.25 range, the error associated to the test dose was >25%, the dose response curve determined from laboratory regeneration doses did not intersect with the natural signal. In such a way, less than 4% of the grains could be used for D_e evaluation (Table 4, 5th column).

The radial plots and the distributions of the individual D_e obtained for the 10 mortar samples are visualized in Fig. 2 (Palazzo Raimondi) and Fig. 3 (Palazzo Soldi), showing a high dispersion with D_e values up to hundreds of Gy. These data were elaborated to get the best estimate of the sample's D_e according to the various statistical models. The D_e results obtained with the weighted mean

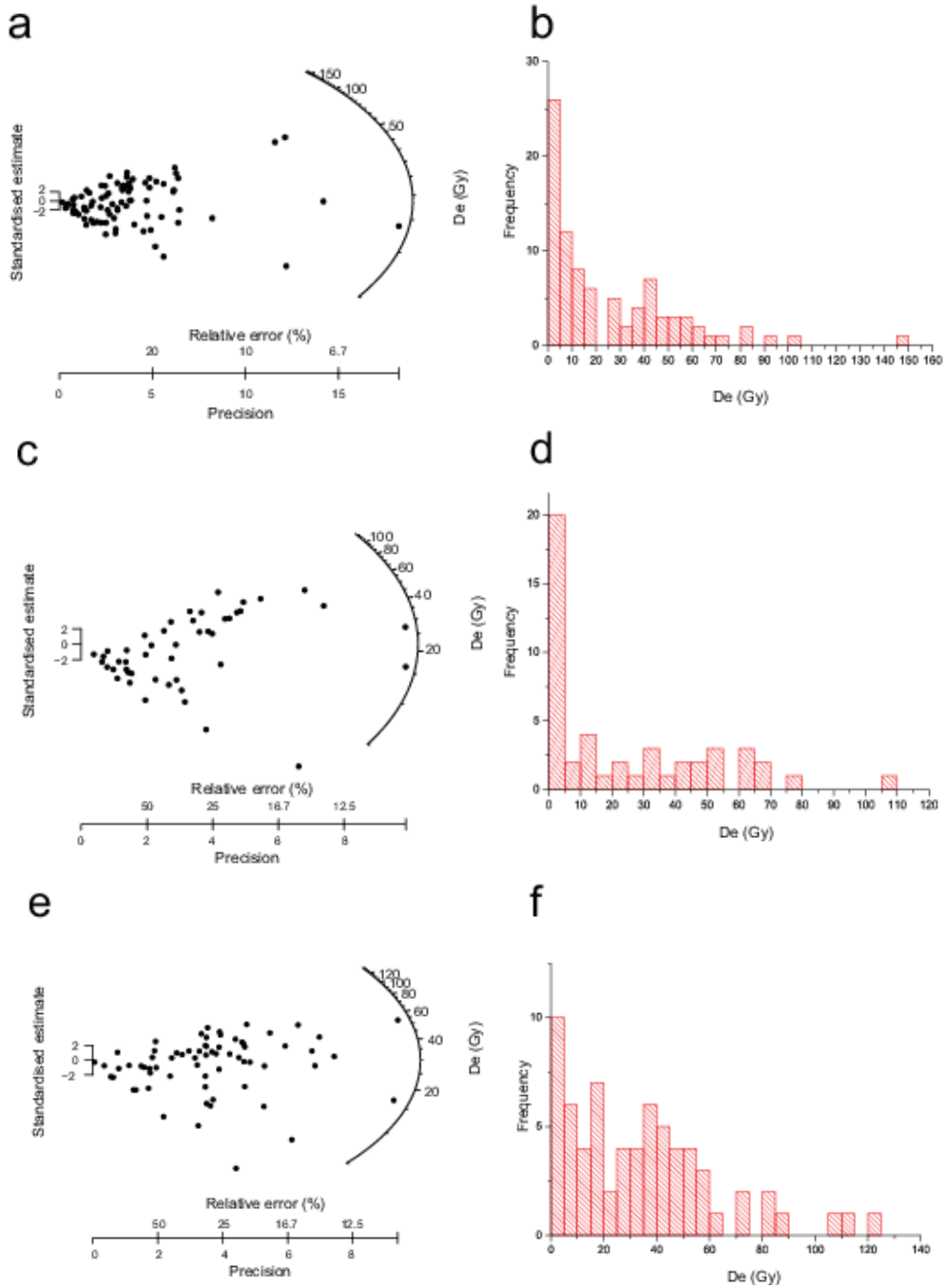


Fig. 2 a-f. Radial plots and histograms of D_e distribution for the mortar samples of Palazzo Raimondi (a and b: PR_1C; c and d: PR_1D; e and f: PR_2C).

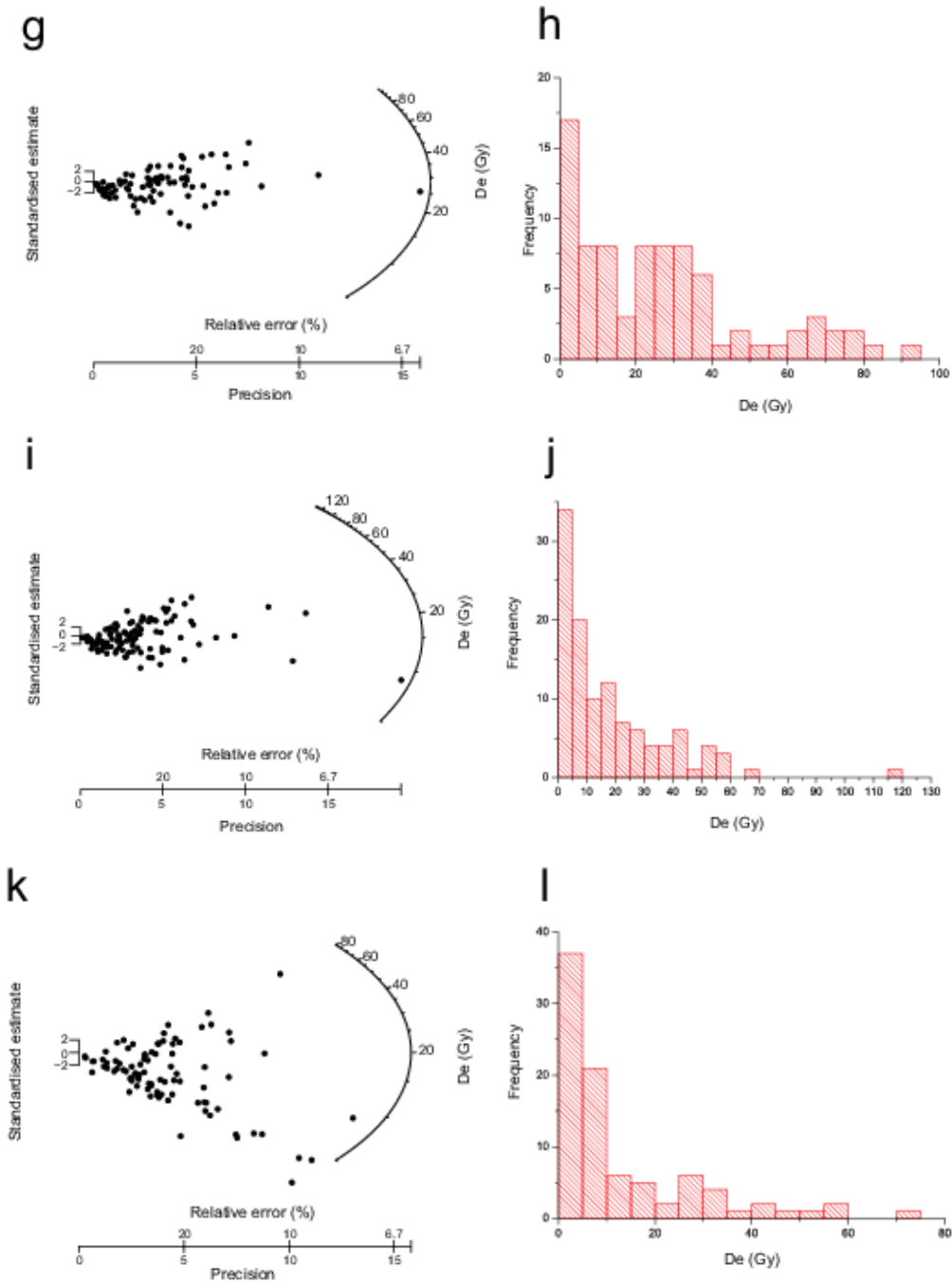


Fig. 2 g–l. Radial plots and histograms of D_e distribution for the mortar samples of Palazzo Raimondi (g and h: PR_2D; i and j: PR_3C; k and l: PR_3D).

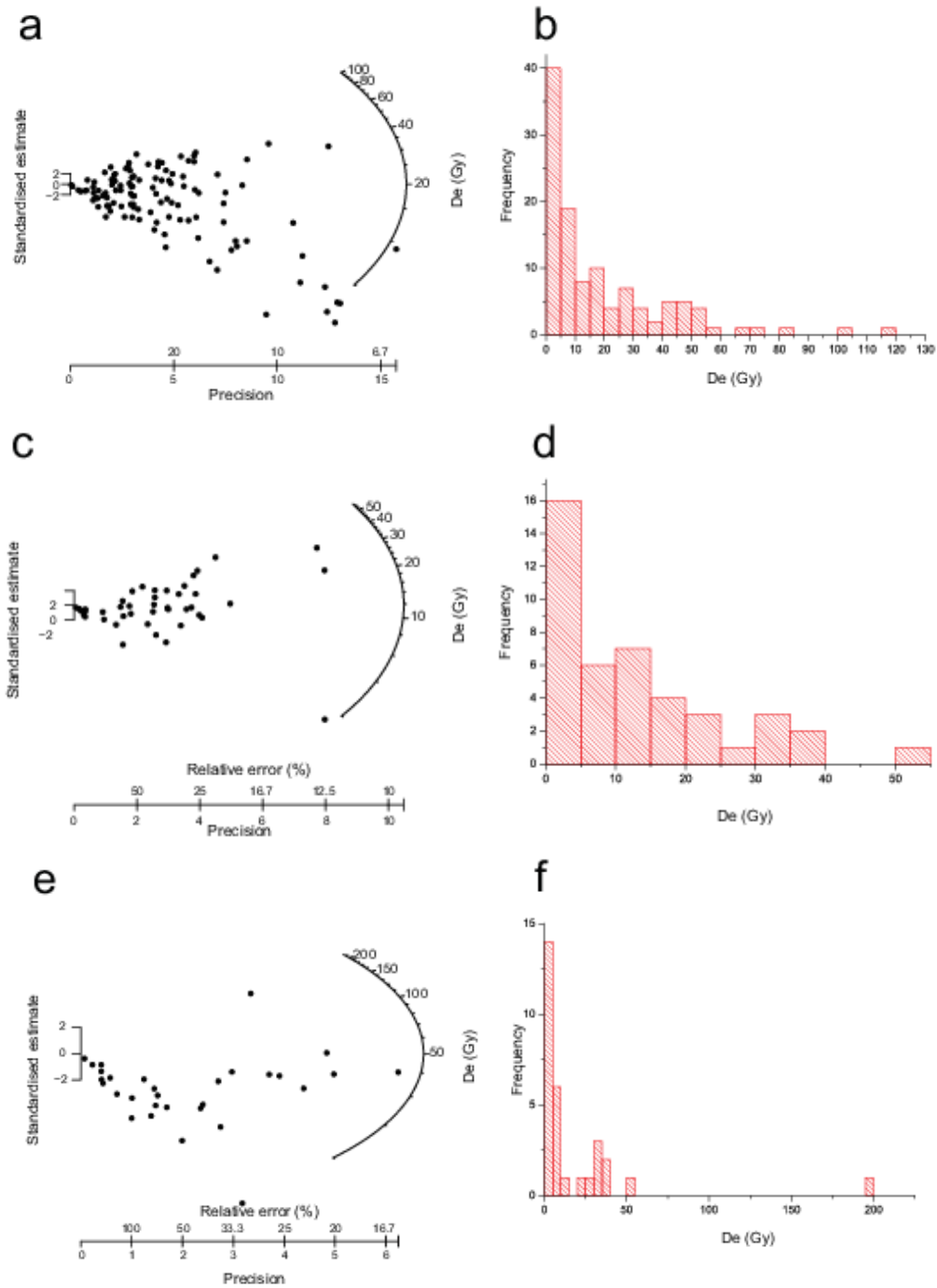


Fig. 3 a–f. Radial plots and histograms of D_e distribution for the mortar samples of Palazzo Soldi (a and b: PS_1C; c and d: PS_2C; e and f: PS_3C).

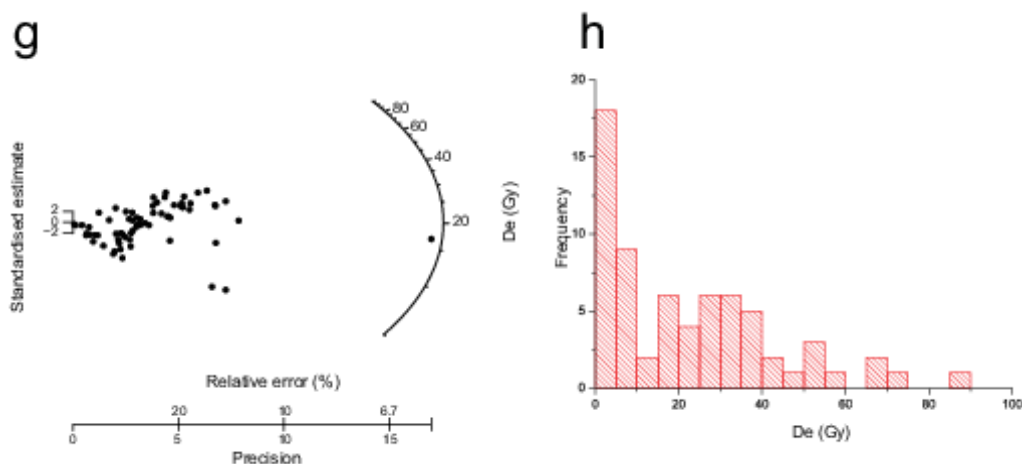


Fig. 3 g–h. Radial plots and histograms of D_e distribution for the mortar samples of Palazzo Soldi (g and h: PS_3D).

Table 4. Single-grain technique: expected D_e and D_e evaluations with different statistical models.

1	2	3	4	5	6	7	8	9	10	11	12
Sample	Expected D_e (Gy)	# Measured grains	# Bright grains (%)	# Accepted grains (%)	OD $D_e^{(a)}$ (%)	OD $D_{rt}^{(b)}$ (%)	D_e Weighted mean (Gy)	D_e CAM (Gy)	D_e MAM (Gy)	D_e ul-MAM (Gy)	D_e IEU (Gy)
PR_1C	1.13	4800	18	1.8	128	19	2.9±0.12	13.4±2.0	2.0±0.4	1.1±0.2	1.08 0.16
PR_1D	1.12	3800	24	1.3	150	20	4.52±0.05	10.7±2.5	1.4±0.4	1.1±0.2	0.93±0.16
PR_2C	1.26	3800	20	1.2	106	29	2.3±0.2	22.9±3.2	3.1±0.8	1.1±0.3	1.2±0.2
PR_2D	1.23	4100	22	2.0	81	20	2.6±0.2	22.0±2.3	6.7±1.2	ND	0.5±0.2
PR_3C	1.09	4200	23	2.6	99	30	2.85±0.12	12.2±1.3	3.5±0.7	1.0±0.3	0.52±0.15
PR_3D	0.96	4000	19	2.2	91	24	3.12±0.09	8.6±0.9	3.9±0.5	ND	ND
PS_1C	0.53	3200	21	3.6	109	20	3.05±0.07	10.6±1.2	2.1±0.3	1.6±0.2	1.6±0.14
PS_2C	0.58	4700	14	0.9	91	30	1.39±0.13	9.9±1.7	2.5±0.7	ND	0.57±0.18
PS_3C	0.64	4200	15	0.7	137	20	1.2±0.2	8.6±2.5	1.5±0.6	0.9±0.2	0.9±0.2
PS_3D	0.62	3900	21	1.7	109	20	3.06±0.17	14.9±2.2	2.8±0.6	1.0±0.2	1.1±0.2

^(a) Over-dispersion of the archaeological D_e .

^(b) Over-dispersion of the samples obtained with a dose recovery experiment. See text for details.

are from to 2 to 5 times higher than expected, the mean error being about 6%. The CAM (Table 4, column 9th) gives results approximately 10 to 20 times higher than expected, with higher errors (10–30%). The over-dispersion parameter (OD) is also reported in Table 4, column 6th. It corresponds to the standard deviation value of the CAM D_e (Galbraith *et al.*, 1999). The intrinsic D_e over-dispersion, required for the application of both the Minimum Age Model and the Internal-External Consistency, is also shown in Table 4, column 7th. It was measured with the dose recovery test (Urbanova *et al.*, 2015). The grains were individually bleached by double green light illumination intercalated to a 10000 s pause. A known beta dose (2.58 ± 0.05 Gy) was given to the sample and subsequently measured. The OD values so obtained varied between 20 and 30%, being considerably

lower than the over-dispersion of the archaeological D_e (see Table 4, 6th column). The contribution of the extrinsic factors to the OD is therefore consistent, indicating the incomplete bleaching as the responsible of the observed huge spread of D_e .

The results of the MAM (column 10th Table 4) were always higher than expected while those of un-logged MAM (column 11th Table 4) were consistent ($\pm 1\sigma$) with the expected ones for five samples out of ten. The same was found with the IEU model (column 12th Table 4), for which the OD calculated with the dose recovery test was added in quadrature to the uncertainties of each individual D_e (Thomsen *et al.*, 2012, 2007 and 2003). All the D_e results of Table 4, normalized to the expected D_e , are visualized in Fig. 4a, grouped by method. Fig. 4b shows only the results of ul-MAM and IEU.

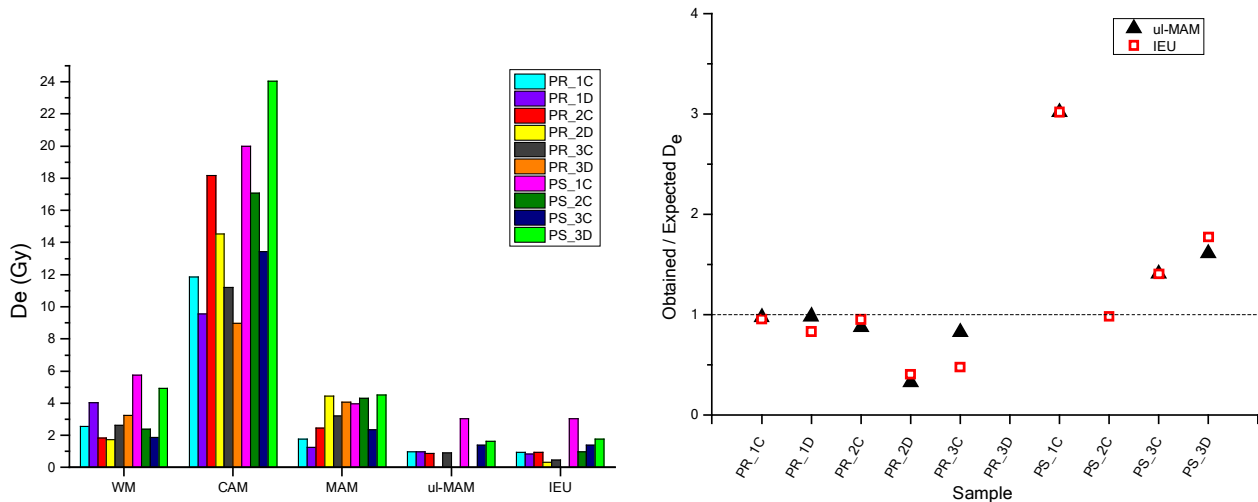


Fig. 4. a) D_e obtained with single-grain technique calculated with different statistical model and normalized to expected D_e . b) D_e results of ul-MAM and IEU.

4. CONCLUSIONS

OSL dating was applied to earthen mortars from Cremona, consisting in a quartz-rich aggregate dispersed in silty-clayey matrix. The aim of this study was to explore the most suitable methods for equivalent dose evaluation for mortars and such an investigation required a set of known age samples. They were taken from two well independently dated structures (Palazzo Raimondi: 1495–1499 AD and Palazzo Soldi: 1770–1790 AD). In this study we applied the multigrain and the single grain protocols for dose evaluation to quartz samples separated from ten well-dated earthen mortars, six from Palazzo Raimondi and four from Palazzo Soldi; the reliability and effectiveness of the various statistical methods in identifying the best-bleached samples were tested. The comparison of the results allows making the following considerations.

The multi-grain protocol gives D_e values higher than expected, leading to a significant and systematic age overestimation. This means that the quartz grains did not receive enough sunlight to fully erase the luminescence signal acquired over geological time. Hence, the resetting process results in an incompletely and heterogeneously reset grain mixture. In order to circumvent this problem, the single-grain protocol was applied. The majority of grains (about 80%) was rejected due to the very low signal-to-noise ratio. Within the analysed grains, after applying the rejection criteria previously described, less than 3.5% were accepted for dose evaluation. The D_e obtained with single-grain procedures showed a large D_e distribution confirming that samples are likely still retaining part of their geological signal. Since D_e are highly dispersed and the samples are very likely affected by heterogeneous bleaching, it is not surprising that D_e were overestimated by the methods including all the dose points (weighted

mean and CAM). The MAM and IEU are therefore expected to better evaluate the true equivalent dose. In many cases the log-MAM3 overestimates the D_e and only for one sample (PR1D) the D_e obtained is in agreement with the expected one. It was found that, in all cases, the un-log MAM3 and IEU model give the better estimation of the mortar expected age, even if the precision of the method is still relatively low.

In conclusion, this study highlighted the potentiality of the OSL single grain technique for mortar dating. At the same time, it revealed the limit of this method to achieve accurate and precise results.

REFERENCES

- Aitken MJ, 1985. *Thermoluminescence dating*. Academic Press, London.
- Aitken MJ, 1998. *An Introduction to Optical Dating*. Oxford University Press.
- Arnold LJ, Roberts RG, Galbraith RF and DeLong SB, 2009. A revised burial dose estimation procedure for optical dating of young and modern-age sediments. *Quaternary Geochronology* 4: 306–325, DOI 10.1016/j.quageo.2009.02.017.
- Aubert JE, Marcom A, Oliva P and Segui P, 2015. Chequered earth construction in south-western France. *Journal of Cultural Heritage* 16: 293–298, DOI 10.1016/j.culher.2014.07.002.
- Bell, 1979. Attenuation factors to absorbed dose in quartz inclusions for thermoluminescence dating. *Ancient TL* 8: 2–13.
- Bonazzi A and Fieni L, 1995. Uso e fortuna delle malte d'argilla nell'Italia Settentrionale: prime ricerche su Cremona. *TeMa Tempo Materia Architettura* 1: 44–53.
- Bøtter-Jensen L, Andersen CE, Duller GAT and Murray AS, 2003. Developments in radiation, stimulation and observation facilities in luminescence measurements. *Radiation Measurements* 37: 535–541, DOI 10.1016/S1350-4487(03)00020-9.
- Bøtter-Jensen L and Murray AS, 2002. Optically stimulated luminescence in retrospective dosimetry. *Radiation Protection Dosimetry* 101: 309–314.
- Cantù M, Giacometti F, Landi A, Riccardi MP, Tarantino SC and Grimoldi A, 2016. Earthen mortars from Cremona (Northern Italy): the evolution throughout centuries of a manufacturing

- tradition. *Construction and Building Materials* 125: 520–532, DOI 10.1016/j.conbuildmat.2016.07.139.
- Cantù M, Giacometti F, Landi AG, Riccardi MP, Tarantino SC and Grimoldi A, 2015. Characterization of XVIIIth century earthen mortars from Cremona (Northern Italy): Insights on a manufacturing tradition. *Materials Characterization* 103: 81–89, DOI 10.1016/j.matchar.2015.03.018.
- Duller GAT, 2003. Distinguishing quartz and feldspar in single grain luminescence measurements. *Radiation Measurements* 37: 161–165, DOI 10.1016/S1350-4487(02)00170-1.
- Duller GAT, Bøtter-Jensen L and Murray AS, 2000. Optical dating of single sand-sized grains of quartz: Sources of variability. *Radiation Measurements* 32: 453–457, DOI 10.1016/S1350-4487(00)00055-X.
- Fieni L, 1999. Approfondimenti metodologici e tecnologici per lo studio delle malte di terra: l'esempio dei manufatti cremonesi. *Archeologia dell'architettura. Supplemento ad Archeologia medievale* XXV 4: 9–28.
- Fratini F, Pecchioni E, Rovero L and Tonietti U, 2011. The earth in the architecture of the historical centre of Lamezia Terme (Italy): Characterization for restoration. *Applied Clay Science* 53: 509–516, DOI 10.1016/j.clay.2010.11.007.
- Galbraith RF, Roberts RG, Laslett GM, Yoshida H and Olley JM, 1999. Optical dating of single and multiple grains of quartz from Jinnium rock shelter, northern Australia: Part I, experimental design and statistical models. *Archaeometry* 41: 339–364, DOI 10.1111/j.1475-4754.1999.tb00987.x.
- Galli A, Martini M, Maspero F, Panzeri L and Sibilia E, 2014. Surface dating of bricks, an application of luminescence techniques. *The European Physical Journal - Plus* 129: 101–109, DOI 10.1140/epjp/i2014-14101-8.
- Goedicke C, 2003. Dating historical calcite mortar by blue OSL: Results from known age samples. *Radiation Measurements* 37:409–415, DOI 10.1016/S1350-4487(03)00010-6.
- Goedicke C, 2011. Dating mortar by optically stimulated luminescence: A feasibility study. *Geochronometria* 38: 42–49, DOI 10.2478/s13386-011-0002-0.
- Guérin G, Mercier N and Adamiec G, 2011. Dose-rate conversion factors: Update. *Ancient TL* 29: 5–8.
- Hale J, Heinemeier J, Lancaster L, Lindroos A and Ringbom Å, 2003. Dating ancient mortars. *American Scientist* 91: 130–137.
- Heinemeier J, Jungner H, Lindroos A, Ringbom A, Von Konow T and Niels R, 1997. AMS ^{14}C dating of lime mortar. *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms* 123: 487–495, DOI 10.1016/S0168-583X(96)00705-7.
- Jain M, Thomsen KJ, Bøtter-Jensen L and Murray AS, 2004. Thermal transfer and apparent-dose distributions in poorly bleached mortar samples: Results from single grains and small aliquots of quartz. *Radiation Measurements* 38: 101–109, DOI 10.1016/j.radmeas.2003.07.002.
- Konow T and Lindroos A, 1997. Dating of lime mortar – Preparation of the sample, a challenge for the geologist and the mineral chemist. *Iskos* 11: 208–213.
- Lapp T, Jain M, Thomsen KJ and Murray AS, 2012. New luminescence measurement facilities in retrospective dosimetry. *Radiation Measurements* 47: 803–808, DOI 10.1016/j.radmeas.2012.02.006.
- Lindroos A, Orsel E, Heinemeier J, Lill JO and Gunnelius K, 2014. Radiocarbon dating of Dutch mortars made from burned shells. *Radiocarbon* 56: 959–968, DOI 10.2458/56.16508.
- Lubritto C, Caroselli M, Lugli S, Marzaioli F, Nonni S, Marchetti Dori S and Terrasi F, 2015. AMS radiocarbon dating of mortar: The case study of the medieval UNESCO site of Modena. *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms* 361: 614–619, DOI 10.1016/j.nimb.2015.05.015.
- Martini M and Sibilia E, 2006. Absolute dating of historical buildings: the contribution of thermoluminescence (TL). *Journal of Neutron Research* 14: 69–74.
- Medialdea A, Thomsen KJ, Murray AS and Benito G, 2014. Reliability of equivalent-dose determination and age-models in the OSL dating of historical and modern palaeoflood sediments. *Quaternary Geochronology* 22: 11–24, DOI 10.1016/j.quageo.2014.01.004.
- Mejdahl V, 1985. Thermoluminescence dating based on feldspars. *Nuclear Tracks and Radiation Measurements (1982)* 10: 133–136, DOI 10.1016/0735-245X(85)90019-5.
- Murray AS and Roberts RG, 1997. Determining the burial time of single grains of quartz using optically stimulated luminescence. *Earth and Planetary Science Letters* 152: 163–180, DOI 10.1016/S0012-821X(97)00150-7.
- Murray AS and Wintle AG, 2000. Luminescence dating of quartz using an improved single-aliquot regenerative-dose protocol. *Radiation Measurements* 32: 57–73, DOI 10.1016/S1350-4487(99)00253-X.
- Murray AS and Wintle AG, 2003. The single aliquot regenerative dose protocol: Potential for improvements in reliability. *Radiation Measurements* 37: 377–381, DOI 10.1016/S1350-4487(03)00053-2.
- Panzeri L, 2013. Mortar and surface dating with Optically Stimulated Luminescence (OSL): Innovative techniques for the age determination of buildings. *Il nuovo cemento* 4: 205–216.
- Pesce GLA, Ball RJ, Quarta G and Calcagnile L, 2012. Identification, extraction, and preparation of reliable lime samples for ^{14}C dating of plasters and mortars with the "pure lime lumps" technique. *Radiocarbon* 54: 933–942.
- Prescott JR and Hutton JT, 1994. Cosmic ray contributions to dose rates for luminescence and ESR dating: Large depths and long-term time variations. *Radiation Measurements* 23: 497–500, DOI 10.1016/1350-4487(94)90086-8.
- Preusser F, Degering D, Fuchs M, Hilgers A, Kadereit A, Klasen N, Krbetschek M, Richter D and Spencer JQG, 2008. Luminescence dating: basics, methods and applications. *Quaternary Science Journal* 57: 95–149.
- Ringbom Å, 1997. The churches of the Åland islands and ^{14}C dating of mortar, Method and theory in Historical Archaeology, Medieval Europe Brugge: pp. 103–122.
- Ringbom Å, Lindroos A, Heinemeier J and Sonck-Koota P, 2014. 19 years of mortar dating: Learning from experience. *Radiocarbon* 56: 619–635, DOI 10.2458/56.17469.
- Thomsen KJ, Jain M, Bøtter-Jensen L, Murray AS and Jungner H, 2003. Variation with depth of dose distributions in single grains of quartz extracted from an irradiated concrete block. *Radiation Measurements* 37: 315–321, DOI 10.1016/S1350-4487(03)00006-4.
- Thomsen KJ, Murray A and Jain M, 2012. The dose dependency of the over-dispersion of quartz OSL single grain dose distributions. *Radiation Measurements* 47: 732–739, DOI 10.1016/j.radmeas.2012.02.015.
- Thomsen KJ, Murray AS, Bøtter-Jensen L and Kinahan J, 2007. Determination of burial dose in incompletely bleached fluvial samples using single grains of quartz. *Radiation Measurements* 42: 370–379, DOI 10.1016/j.radmeas.2007.01.041.
- Urbanová P, Hourcade D, Ney C and Guibert P, 2015. Sources of uncertainties in OSL dating of archaeological mortars: The case study of the Roman amphitheatre "palais-Gallien" in Bordeaux. *Radiation Measurements* 72: 100–110, DOI 10.1016/j.radmeas.2014.11.014.
- Urbanová P and Guibert P, 2017. Methodological study on single grain OSL dating of mortars: Comparison of five reference archaeological sites. *Geochronometria* 44: 77–97, DOI 10.1515/geochr-2015-0050.
- Wintle AG and Murray AS, 2006. A review of quartz optically stimulated luminescence characteristics and their relevance in single-aliquot regeneration dating protocols. *Radiation Measurements* 41: 369–391, DOI 10.1016/j.radmeas.2005.11.001.
- Zacharias N, Mauz B, Michael CT, Horowitz YS and Oster L, 2002. Luminescence quartz dating of lime mortars. A first research approach. *Radiation Protection Dosimetry* 101: 379–382.