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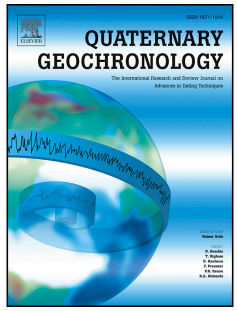

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Mortar OSL and brick TL dating: the case study of the UNESCO world heritage site of Modena

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Keywords

Bricks, mortars, TL, OSL, dating

Highlights

Evidence of reuse of Roman bricks from the comparison of TL and OSL dating results

Uncompleted bleaching of the OSL signal of mortar

Abstract

In this study, TL and OSL dating were applied respectively to bricks and mortars taken from a few key structures of the UNESCO World Heritage Site of Modena (northern Italy). The samples came from the Cathedral and the Ghirlandina Tower, built between the end of the XII century and the first half of the XIV century AD.

TL dating of bricks showed that we were dealing with the well-known phenomenon of re-use of ancient Roman bricks. However, it was also possible to discover and date quite precisely a previously unknown renovation phase in the Cathedral apse area (XVI century). Regarding the OSL mortar dating, both Multi-Grain and Single Grain techniques were applied on quartz

grains, possibly well bleached during mortar preparation. OSL gave good results for one sample from the Cathedral and three from the Ghirlandina Tower. The other gave ages much older than expected, indicating the possible uncompleted bleaching of the quartz grains as the main problem of this dating application. Finally, the application of the Bayesian statistical approach, reducing the error associated with the data, supported a new building chronology, in particular for the Ghirlandina Tower.

1. Introduction

In recent years the retrospective dosimetry using quartz extracted from mortar sand aggregate has been developed after noticing that quartz grains are bleached during mortar manufacturing and are therefore suitable to be used as a dosimeter (Bøtter-Jensen et al., 2000). Although some attempts were made to find reliable Optically Stimulated Luminescence (OSL) dating protocols (Zacharias et al, 2002, Goedicke, 2003, Goedicke, 2011, Panzeri, 2013, Stella et al., 2013; Urbanova et al., 2015, Urbanovà et al. 2016, Urbanovà and Guibert, 2017, Panzeri et al., 2017), OSL mortar dating is not a routine method so far. In particular, the main issue is that the quartz grains contained in the mortar may be only partially or inhomogeneously bleached leading to an overestimation of the sample age. The development of the Single Grain technique (Bøtter-Jensen and Murray, 2002; Murray and Roberts, 1997) allowed a better identification of the well bleached quartz grains, which represent a fundamental step for reliable dating. However, the identification of the bleached grains is not always successful, indicating that further investigations might be needed to assess the dating protocol.

The UNESCO World Heritage Site of Modena represents a good case for the application of absolute dating techniques, because of the availability of historical information and the accessibility to the key structures for sampling. The historical documents date the foundation of the Cathedral (1099) and the completion of the Ghirlandina bell tower (1319), while there are conflicting interpretations on the dates of the construction phases (Peroni, 1999; Silvestri, 2013). This work is part of a wide project for the scientific characterization of the construction materials of the monuments (Lugli et al., 2010, Lugli et al 2011 and Lugli et al., in press), including an AMS radiocarbon dating campaign on lime mortars (Lubritto et al. 2015), some of which are still in progress.

This paper illustrates the TL and OSL dating results of nine samples of bricks and mortars from the Cathedral and the Ghirlandina Tower in the framework of the main hypotheses about the construction phases (Peroni, 1999, Labate 2010, Silvestri, 2013), and a comparison with the presently available radiocarbon data (Lubritto et. al., 2015).

2. Sampling and methodology

Five bricks with the associated mortars were sampled from the Cathedral (MD1-5 brick, and MD1-5 mortar), and four from the Ghirlandina Tower (MG1-4 brick, MG1-4 mortar), in order to study the main construction phases (see Fig. 1). Cores of bricks and mortars were extracted from the inner part of the walls avoiding any additional exposure to daylight. Furthermore, all the laboratory procedures were performed under dim red light.

For TL dating of bricks, the polymineral fine grain technique (4-11 μm, Zimmerman, 1971) was used and the Multiple Aliquot Additive Dose (MAAD, Aitken, 1985) protocol was applied to evaluate the Equivalent Dose (D_e). The OSL measurements, following the quartz inclusion technique (Fleming, 1973) with the Single Aliquot Regenerative dose (SAR, Murray and Wintle, 2000) were used, applying both Multi-Grain (MG) and Single Grain (SG) techniques. The 150-250 μm size quartz fractions were extracted according to the standard procedures (Preusser et al., 2008; Mejdahl, 1985), and the absence of feldspars was checked using IR stimulation (830 ± 10 nm; constant stimulation power of 360 $mW/cm^{2)}$. Actually, the only two mortars with sufficient amount of quartz grains to perform both MG and SG techniques were MD5 and MG4.

TL dating was performed using a home-made system equipped with a photomultiplier tube (EMI 9235QB) coupled to a blue filter (Corning BG12). The samples were heated from RT to 480°C at 15°C s^{-1}. Artificial irradiations were carried out by means of a 1.85 GBq ^{90}Sr-^{90}Y beta source (dose-rate: 4.21 Gy min^{-1}) and a 37 MBq ^{241}Am alpha source (dose-rate: 14.8 Gy min^{-1}). OSL measurements were carried out using a Risø TL-DA-20 equipped with a ^{90}Sr/^{90}Y beta source delivering 0.135 Gy s^{-1} to the sample position.

The OSL was stimulated in case of MG technique by an array of blue LEDs (470 ± 30 nm) for 40 s at 125°C with a constant stimulation power of 54 mW cm^{-2}. Individual D_e values were accepted if the following criteria occurred: recycling ratio between 0.9 and 1.1, recuperation < 5%, IR signal < 5%. To get the best estimate of the true value of a sample, the weighted mean was used. The SG analysis were performed by a 10 mV Nd:YVO_4 solid state diode pump laser emitting at 532 nm. The grains were rejected if one of the following conditions was not satisfied: the signal was less than 3 standard deviation above the background, the recycling ratio was out of 0.75-1.25 range, the error associated to the test dose was >25%, the signal of the natural D_e is out of the range of the laboratory regeneration doses. The number of measured and accepted aliquots or grains are reported in Table 1. The individual D_e values were statistically elaborated using the weighted mean for the sample MG4 and the Minimum Age Model (MAM, 3 parameter logaritmic version; Galbraith et al., 1999) in the case of sample MD5 using the Luminescence 0.4.4 package contained in the R software (http://CRAN.R-project.org/package=Luminescence).

Photons were detected by a bialkali photomultiplier tube (EMI 9235QB) coupled to a 7.5 mm Hoya U-340 filter.

For the dose-rates determination, ^{238}U and ^{232}Th concentrations were derived from alpha counting 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 ranged from 12 to 20 % for bricks, and from 8 to 12% for mortars, assuming for calculations an amount of water corresponding to 20 ± 5 % of saturation. The attenuation of the beta particles in coarse grain mortar 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). For each material (brick and mortar) such contribution was evaluated from its own radioactivity and from that of the surrounding environment (Galli et al., 2014), applying the infinite matrix approximation, with updated conversion factors (Guérin et al, 2011).

3. Results and discussion

TL dating results are listed in Table 1. Examples of TL glow curves for the brick samples MD1 and MG4 are reported in Figure 1 together with the corresponding growth of TL signal vs additive doses. Most of the bricks showed an age which is much older than the construction of the cathedral and date back to the Roman age (III-I century BC). It follows that most of the bricks used in the Middle Age were coming from the despoliation of ancient Roman monuments. These data are in agreement with the study of the size of the bricks and of the ornamental stone cover, which is largely composed of reused slabs (Lugli et al., 2009). Only two samples resulted in post-Roman ages (MG4 brick and MD3 brick). In particular, MG4 (brick) was likely produced in the Middle Age, probably after the second half of the 13th century when the despoliation of Roman monuments ceased and new bricks were produced to complete the construction of the tower (1319 AD; Lugli et al., 2009). On the other hand, sample MD3 (brick) shows an age dating back to the16th century, which is younger than the completion of the cathedral. This particular sample is coming from the choir of the cathedral and is associated to fragments of a gypsum mortar binder. These observations suggest that the area was modified in the 16th to fit the new artistic taste of the moment.

Mortar OSL MG technique gave results compatible with the construction phases illustrated by Labate (2009), Peroni (1999) and Silvestri (2013) only for three samples from the Ghirlandina

Tower (MG1 mortar, MG2 mortar and MG4 mortar). All the other samples resulted in ages much older than expected, ranging from the 11th century BC to the 8th century AD. This age overestimation is due to the partial or inhomogeneous bleaching of the quartz grains during the mortar manufacturing process. In fact the E.D. distributions of these samples are not normally distributed and showed a scattering of value with a long tail toward higher doses.It is not clear at present the reason for the partial bleaching of the quartz grains, but Sawakuchi et al., 2011 suggested that vegetated floodplains and permanent flow of turbid waters together with fast transportation reducing the number of episodes of erosion and deposition along the river stream do not favor quartz bleaching. These characteristics are compatible with the sand supply areas of the UNESCO site.

The application of the SG technique to the mortar samples MD5 and MG4 allowed to obtain reliable results. In particular, the application of the MAM to the sample MG4 allowed to overcome the problems of incomplete bleaching.

In Fig.2 the ages of all bricks and mortars samples that gave reliable results are reported together with the only available radiocarbon dating (Lubritto et al., 2015).

To reduce the data uncertainty, the Bayesian statistical approach (Bayes, 1958), combining in a single formal analysis the experimental ages together with the present knowledge of the building chronology, was attempted. This approach is useful when matching multiple dates and prior knowledge about a site. In this case, the known connections between the building phases were used as likelihood parameters integrating prior hypothesis and dating results, including the only available radiocarbon date (MG1 mortar, Lubritto et al., 2015). The results are shown in Fig.3 where both the raw data (light grey areas) and the modelled probabilities after the application of the Bayesian statistics (dark grey areas) are shown. Clearly, the introduction of boundaries regarding historical constraints (foundation of the cathedral and tower completion) narrows the probability density curves (mainly on MD5 and MG2), and allows a more realistic and useful building chronology for the Ghirlandina Tower.

4. Conclusions

The study of mortars and bricks used in the medieval Modena UNESCO site provided us with some significant insights on the reliability of TL and OSL dating techniques in a complex polyphase historical building context. TL was successfully applied to the totality of the bricks samples and the results confirmed the widespread practice to re-use bricks taken from ancient Roman monuments during the Middle Age. The dating of bricks brought to light a previously unknown XVI century renovation of the choir area and the discovery was then confirmed by the detailed study of the wall structure. OSL provided compatible data on mortars in 50% of the cases due to the incomplete or partial bleaching of the quartz grains. The large proportion of partially bleached grains may be related to the characteristics of the sand exploitation areas that are mostly vegetated floodplain sites and rivers with turbid waters providing fast transportation along the riverbeds.

The application of the Bayesian statistics allowed us to narrow the probability density curves providing a more reliable building chronology for the Ghirlandina Tower.

Table caption

Table 1. List of bricks and mortars samples from Cathedral (MD) and Ghirlandina Tower (MG). The table reports: sample code, sample type, dating technique, number of aliquots or grains measured, number of accepted aliquots or grains, D_e, dose rate and date. The data in agreement with the historical information are reported in bold.

Figures captions

Figure 1. TL glow curves for samples MD1 (a) and MG4 (c) and corresponding growth of TL signal vs. additive dose (b and d).

Figure 2. a) Construction phases of the Cathedral after Peroni 1999 and Caroselli 2015 (sample MD3 and 5 are from the interior of the cathedral); b) Construction phases of the Ghirlandina Tower after Labate 2010.

Figure 3. Probability density curves of Cathedral and Tower samples dating. The probability distributions before the Bayesian statistics are reported in light grey, the modelled probabilities and data ranges are reported in dark grey. The two chronological constraints given by the cathedral foundation and tower completion are also shown (Bronk 2009).

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Table 1.

Sample code	**Sample type**	**Technique**	**# Measured aliquots/grains***	**# Accepted aliquots/grains ***	**De (Gy)**	**Dose rate (mGy/a)**	**Date**
MD1	Brick	TL			10.0 ± 0.5	4.69 ± 0.14	120 BC ± 125
MD1	Mortar	OSL MG	20	15	2.1 ± 0.1	1.67 ± 0.08	770 AD ± 70
MD2	Brick	TL			12.5 ± 0.6	5.73 ± 0.17	175 BC ± 125
MD2	Mortar	OSL MG	12	8	4.8 ± 0.3	1.80 ± 0.09	630 BC ± 150
MD3	Brick	TL			1.7 ± 0.1	3.79 ± 0.11	**1565 AD ± 30**
MD4	Brick	TL			13.9 ± 0.7	6.32 ± 0.19	180 BC ± 130
MD4	Mortar	OSL MG	28	17	3.6 ± 0.2	1.60 ± 0.08	240 BC ± 120
MD5	Brick	TL			9 .0 ± 0.45	4.10 ± 0.12	180 BC ± 130
MD5	Mortar	OSL MG	83	42	2.7 ± 0.1	1.53 ± 0.08	250 BC ± 100
MD5	Mortar	OSL SG	5900	71	1.2 ± 0.4	1.47 ± 0.07	**1210 AD ± 270**
MG1	Brick	TL			14.7 ± 0.7	6.82 ± 0.20	140 BC ± 110
MG1	Mortar	OSL MG	88	38	1.42 ± 0.06	1.70 ± 0.09	**1180 AD ± 45**
MG2	Brick	TL			10.8 ± 0.5	5.18 ± 0.16	70 BC ± 120
MG2	Mortar	OSL MG	20	10	1.74 ± 0.09	1.75 ± 0.09	**1020 AD ± 60**
MG3	Brick	TL			14 ± 0.7	6.60 ± 0.20	105 BC ± 120
MG3	Mortar	OSL MG	70	37	3.24 ± 0.13	1.07 ± 0.05	1000 BC ± 115
MG4	Brick	TL			3.2 ± 0.16	4.78 ± 0.14	**1345 AD ± 40**
MG4	Mortar	OSL MG	54	35	1.18 ± 0.06	1.74 ± 0.09	**1340 AD ± 40**
MG4	Mortar	OSL SG	3700	27	1.39 ± 0.13	1.74 ± 0.09	**1220 AD ± 90**

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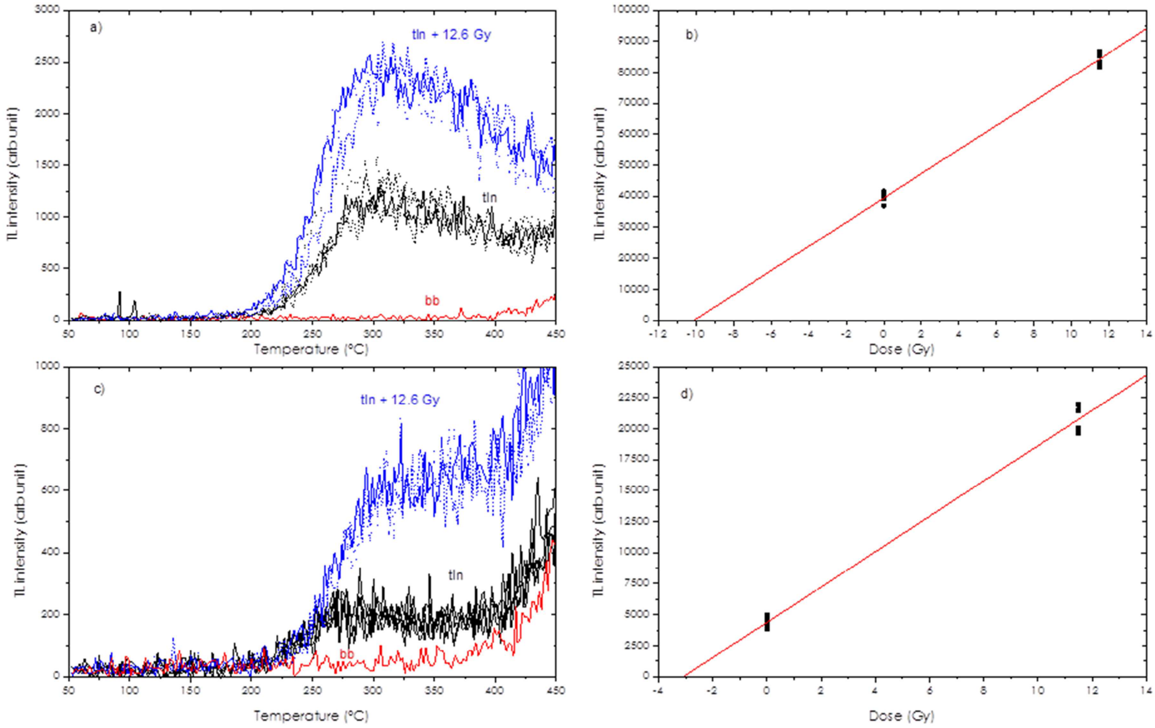
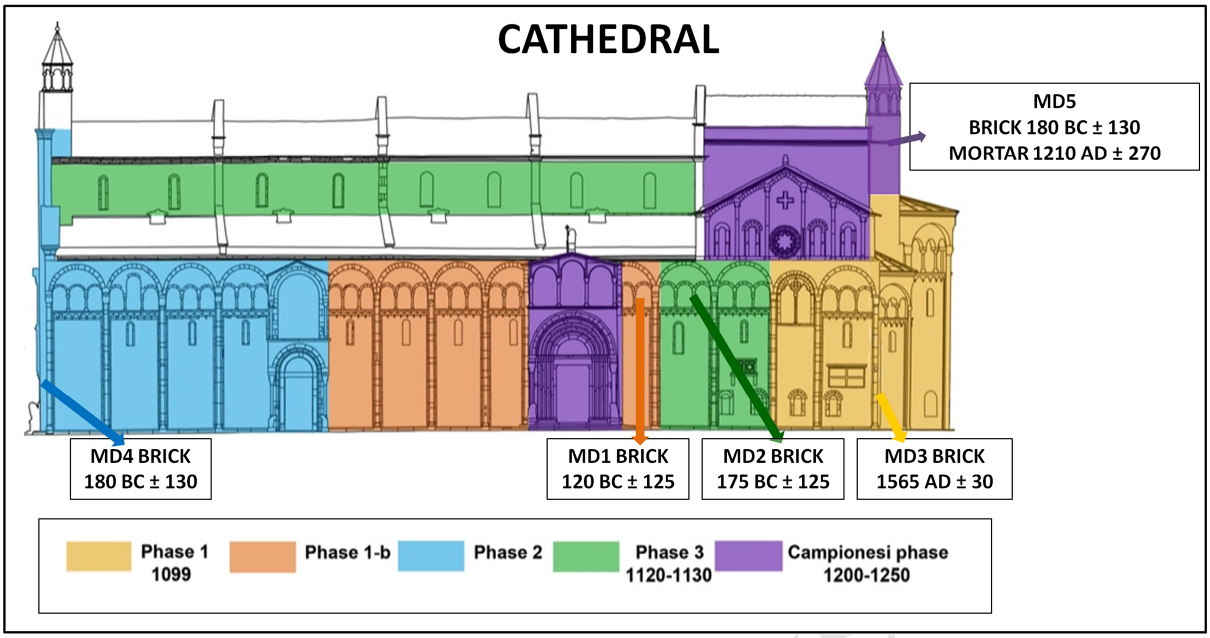
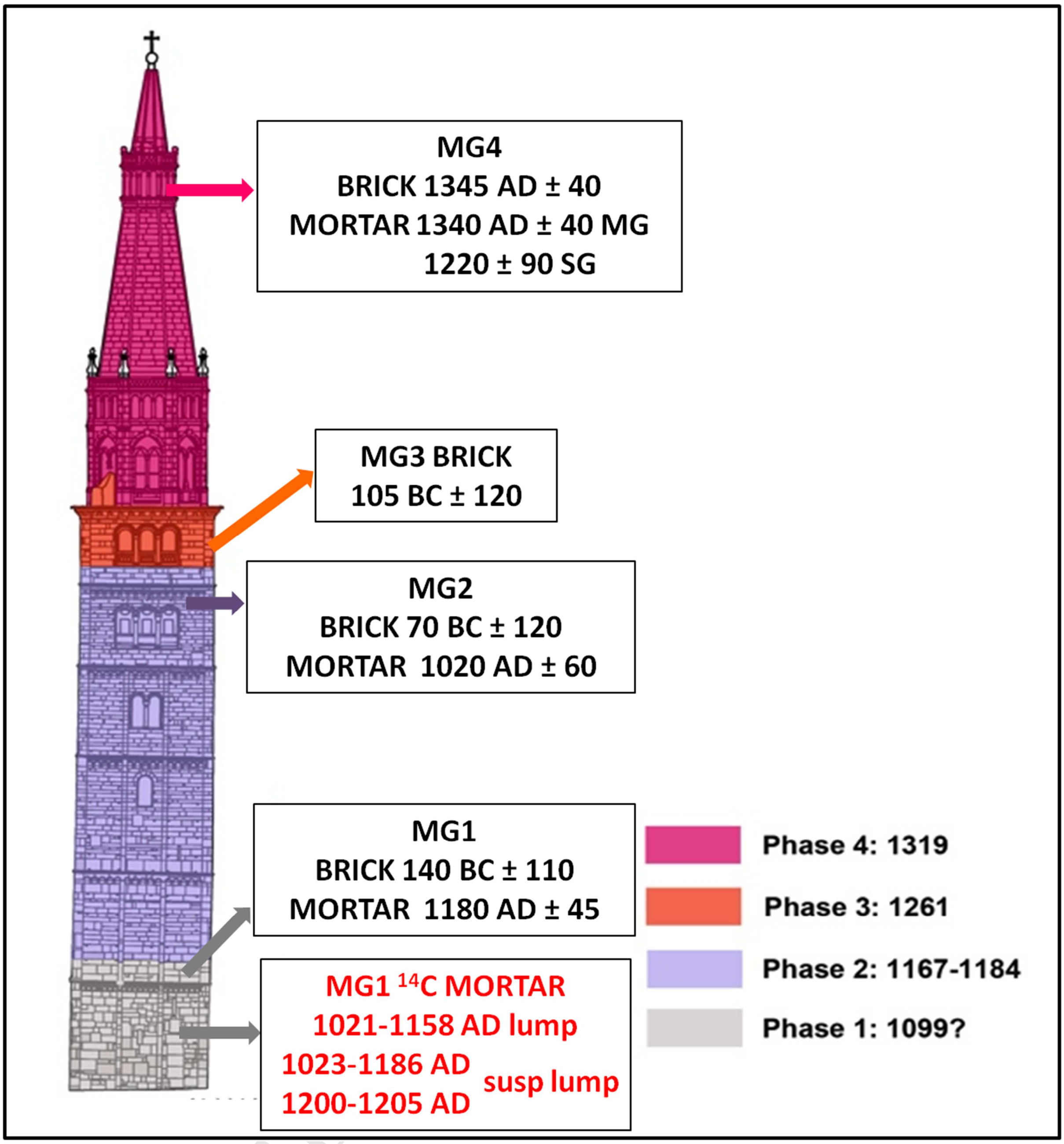
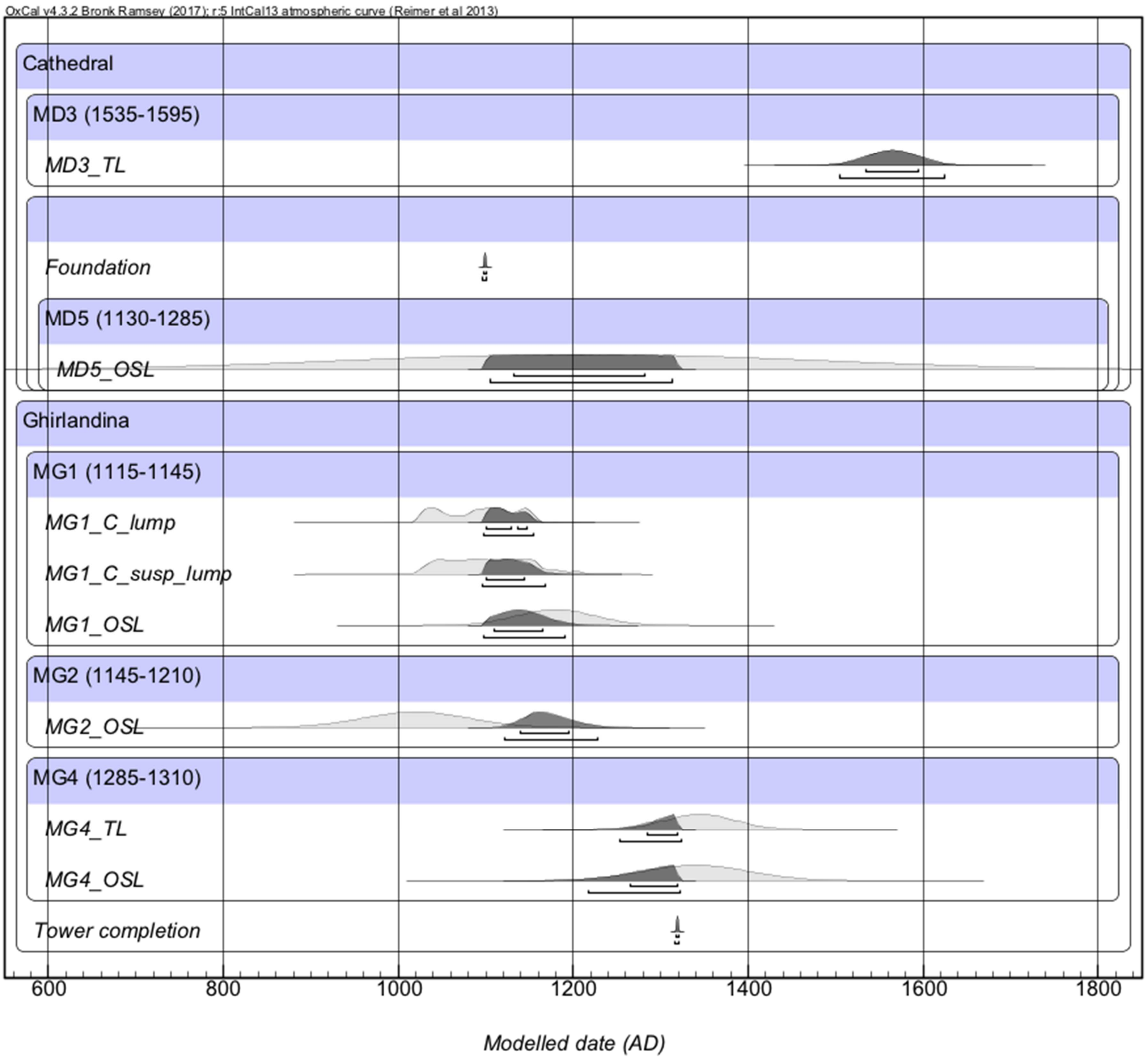


a)
tln + 12.6 Gy
tln
bb
TL intensity (arb unit)
Temperature (°C)
b)
TL intensity (arb unit)
Dose (Gy)
c)
tln + 12.6 Gy
tln
bb
TL intensity (arb unit)
Temperature (°C)
d)
TL intensity (arb unit)
Dose (Gy)


CATHEDRAL
MD5
BRICK 180 BC ± 130
MORTAR 1210 AD ± 270
MD4 BRICK
180 BC ± 130
MD1 BRICK
120 BC ± 125
MD2 BRICK
175 BC ± 125
MD3 BRICK
1565 AD ± 30
Phase 1
1099
Phase 1-b
Phase 2
Phase 3
1120-1130
Campionesi phase
1200-1250



MG4
BRICK 1345 AD ± 40
MORTAR 1340 AD ± 40 MG
1220 ± 90 SG
MG3 BRICK
105 BC ± 120
MG2
BRICK 70 BC ± 120
MORTAR 1020 AD ± 60
MG1
BRICK 140 BC ± 110
MORTAR 1180 AD ± 45
MG1 14C MORTAR
1021-1158 AD lump
1023-1186 AD
1200-1205 AD
susp lump
Phase 4: 1319
Phase 3: 1261
Phase 2: 1167-1184
Phase 1: 1099?


OxCal v4.3.2 Bronk Ramsey (2017); r:5 IntCal13 atmospheric curve (Reimer et al 2013)
Cathedral
MD3 (1535-1595)
MD3_TL
Foundation
MD5 (1130-1285)
MD5_OSL
Ghirlandina
MG1 (1115-1145)
MG1_C_lump
MG1_C_susp_lump
MG1_OSL
MG2 (1145-1210)
MG2_OSL
MG4 (1285-1310)
MG4_TL
MG4_OSL
Tower completion
600
800
1000
1200
1400
1600
1800
Modelled date (AD)