Sampling problems in the radiocarbon dating of old mortars and plasters with the “pure lime lumps” technique

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1. Introduction

Several scientific papers describe the radiocarbon dating of lime mortars and plasters [Folk and Valastro, 1976; Van Strydonck et al., 1992; Hale et al., 2003; Nawrocka et al., 2005]. In many cases, these lime based mixtures are dated by using pieces of organic materials contained within the mix such as charcoal, wood or straw. However, this type of application can only provide post-quem chronological information. The results obtainable, in fact, are not connected with the hardening process of lime but with the formation process of the organic material embedded in the mixture and this can be a quite important limitation, in the archaeological interpretation of the results obtained by radiocarbon dating.

Rarer and with not yet fully reproducible results are the papers dealing with the radiocarbon dating of calcium carbonate contained in the mortars as binder phase. In this case, the ^{14}C dating is carried out directly on the calcium carbonate precipitated during the hardening process of lime by the reaction between calcium hydroxide and atmospheric carbon dioxide. As the content of ^{14}C contained in the newly formed calcium carbonate reflects the ^{14}C concentration in the atmosphere at the time of hardening, this material can be used for the radiocarbon dating of old mortars and plasters.

Although the method is quite simple in its basis principle, relevant issues come from the contamination problems of the dated samples with other carbon sources. Grains of carbonate sand or underburned pieces of the same limestone used to produce the lime, that are originally mixed with the binder cannot be, in fact, completely removed from the mixtures. These materials do not contain radioactive carbon[1] but behave as the carbonated lime during the analyses. For this reason the radiocarbon dating of old lime-based mixtures has not yet been used intensively over the past decades.

Over the past years, this problem led to the development of new techniques for the sample preparation (e.g. Sonninen and Junger, 2001) and among these techniques, the so called “pure lime lumps” represents a fast and reliable method. The technique is based on the use of lumps of pure lime, very often embedded in old lime based mixtures as material for the radiocarbon dating. Because these lumps are made of pure lime [Bugini and Toniolo, 1990] any contamination problem is avoided [Pesce and Ball, 2012]. However, despite the remarkable results already achieved with this technique [Pesce et al., 2009; Pesce et al., 2012; Pesce et al., 2013], the sample collection is still a very important issue for a successful application of the radiocarbon dating.

This paper describes the main sampling problems faced during a research on

the accuracy and precision of the "pure lime lumps" technique, founded by the University of Genoa[2] and carried out together by the University of Genoa and the and CEDAD in Italy and the University of Bath in United Kingdom. Results of this research were presented at the 21st International Radiocarbon Conference, held in Paris from the 9th to the 13th July 2012.

2. The case study

The wall chosen for carrying out the research is the façade of a medieval building in "Vico delle Fate" in Genoa (Italy). The building is located in the urban area called "Colle", close to one of the doors originally opened in the medieval city wall (the so called "Porta Soprana"). This façade was chosen because the following reasons:

• it is part of a territorial compound well known from an archaeological and historical point of view. In particular, this area is rich in chronological landmarks not necessarily related to the dating methods used during the test such as written documents and cartographies gathered together in the archives;

• it allows the use of different absolute dating methods. Methods that can be used both, at locale scale such as the so called mensio-chronology of bricks[3] and chrono-typology of mortars[4] and at wider scale such as thermoluminescence of bricks and radiocarbon dating of mortars;

• it has a visible structure (e.i. free from renders) made of bricks laid on thick mortar joints where an appropriate number of pure lime lumps and other type of samples could be collected and used for both, characterization of the binder and radiocarbon dating;

• despite the several remakes, since the second world war (when the building was abandoned because of a partial collapse) there have not been substantial changes.

3. Results of the stratigraphic analysis

The stratigraphic analysis of the façade allowed the recognition and the study of almost 200 stratigraphic units (SU), attributed to about ten construction activities occurred over the past six centuries.

According to the results obtained at the end of the archaeological analysis, the first building was characterized by a loggia at the ground floor opened on Vico delle Fate, by a mullioned window at first floor and a row of small suspended arches between the ground floor and the first floor (very common in the medieval architecture of Genoa). The last phase that has been recognized is, instead, the temporary arrangement set up by the "Genio Civile"[5] after the bombardment of 1943 in order to prevent collapse that could have been dangerous for the people walking along Vico delle Fate.

Between these two phases it has been possible to recognize others changes and, in particular, a phase when the loggia was closed as well as the mullioned windows, while the small suspended arches were filled with lime mortar and bricks. At the same time, a door with a marble frame was opened at the ground floor in order to have once again access to Vico delle Fate. At the first floor, two rectangular windows were opened in place of the mullioned window. A later architectural solution added the shutters to the rectangular windows

Stratigraphic unit	Structure	Dating based on the size of the bricks (AD)
9	Wall plug built to close the loggia	1505-1654
17	Wall plug built to close the loggia	1450-1690 (most likely 1510 or 1600-1610)
		1150-1200
15	Pillar of the loggia	1260-1610 (most likely 1290-1310 or 1450-1475)
20	Arches on the pillar SU 15	1260-1610 (most likely 1450-1460 or 1510-1570)

Table 1 - Results of the mensio-chronology dating of bricks for the main SU identified in the façade

and a render on the whole façade that was decorated with lime based paint and very simple architectural motifs including painted windows frames.

4. Result of the absolute dating

The low cost of the absolute dating methods applicable on local scale such as the mensio-chronology of bricks and chrono-typology of mortars, allowed quite wide applications and, consequently, allowed to collect a large number of chronological information. This extensive dating work has been useful for improving the results of the stratigraphic analysis and for characterizing of the main constructive phases. Differently, the absolute dating methods such as the thermoluminescence and the radiocarbon dating have been only used in the SU belonging to the first constructive phase and, in particular, in the loggia opened on Vico delle Fate.

Overall, the analysis of the size of the bricks allowed dating of twelve SU[6]. Results of this dating method show a quite broad range of dating spread from the 13th to the 19th century AD. The results for the main SUs are reported in table 1. These data suggest that the loggia was built between the mid of the 13th century and the beginning of the 17th century AD (SU 15 and 20).

In agreement with the results of the stratigraphic analysis, the mensio-chronology dating of the bricks used in the wall plug that was built to close the loggia, date these materials between the end of the 15th and the end of the 17th century AD (SU 9 and 17). Interestingly, within the bricks of the SU 17, some bricks older than the other, dated between the 1180 and the 1250 AD were found. This suggested the reuse of some old building materials in the construction of the wall plug.

Chrono-typology of mortars allowed dating several SU. Samples were analysed by the geologist Roberto Ricci using a stereo optical microscope with magnification up to 50x, equipped with a source of cold light and fibre optics. The analysis allowed identifying three main areas of provenance where the sand was extracted: the sector 3/5 of the beaches close to the city centre of Genoa (where the shore is no more accessible); the Sampierdarena's beach (an area west of the city centre) and the Po valley (the widest valley in the northern Italy).

According to the results of the researches carried out over the past forty years at the University of Genoa and at the Institute of the History of Material Culture, the sand extracted in the sector 3/5 was used between the 11th and the 14th century AD. The sand extracted near Sampierdarena was used between the 15th and the 19th century, while the sand extracted in the Po valley has been

Sample n.	Structure	Calibrated result (AD)	Confidence interval
2	Arch above the pillar	1280-1400	95.4%
4	Pillar of the loggia	1270-1400	95.4%
5	Pillar of the loggia	1280-1410	95.4%
6	Pillar of the loggia	1490-1690 1730-1810 1920-1960	63.6% 24.4% 7.4%
7	Pillar of the loggia	1270-1420	95.4%
8	Masonry between the arches above the pillar	1180-1310 1350-1390	89.1% 6.3%
12a	SU 17 - Wall plug built to close the loggia	1150-1290 1050-1080	93.3% 2.1%

Table 2 - Results of the radiocarbon dating of the lime lumps sampled in the façade

used in Genoa since the 1860 AD, when the railway that connect Genoa with the Po valley was built. Because it has been found that the mortars sampled in the loggia contained sand from sector 3/5, the construction time of this structure can be dated between the 11th and the 14th century AD. The mortars sampled in the wall plug that closed the loggia contained sand from Sampierdarena and this suggests that the construction time of these masonries has to be dated between the 15th and the 19th century AD.

The radiocarbon dating[7] was used to date 7 lumps of pure lime: 4 lumps were sampled in the mortar used in a pillar of the loggia (samples n. 4, 5, 6 and 7); 1 lump was taken in the arch above the pillar (sample n. 2); 1 lump in the masonry between the two arches above the pillar (sample 8) and 1 lump in a wall plug that closed the loggia (sample 12a). Results are reported in table 2 and show a very good consistency among the samples 2, 4, 5 and 7 dated between the 1270 AD and the 1420 AD. Sample 6, despite the fact that was taken in the same pillar of the samples 2, 4, 5 and 7, is dated to a later time which is compatible with the construction time of the wall plug that closed the loggia. Sample 8 is dated between the 1180 and the 1310 (89.1% confidence interval): a time compatible with the result of the sample 12a and with thermoluminescence results.

The thermoluminescence dating method[8] was applied to a couple of fragments coming from the same brick used in the pillar of the loggia. Results date the two samples to the 823-1303 AD e 688-1288 AD (confidence interval 2σ). Because the samples come from the same brick, it is possible to accept a dating between the 823 and the 1288 AD for the whole brick.

5. Discussion

Overall, from the above mentioned results it is possible to highlight a satisfactory overlap of the dating obtained with the mensio-chronology of the bricks (samples 15 and 20), with the chrono-typology of the mortars and with the radiocarbon dating of lumps 2, 4, 5 and 7. All these results suggest that the loggia was built during the 14th century AD. This is in agreement with the information already available in the archives regarding the urban development of this area during the late middle age and with the architectural characteristics of the building reconstructed by the archaeological analysis (e.i. shape of the arches, masonry technique, etc.). The dating is also consistent with the results

Fig.1 - Details of the sampling points of the lump n. 7 (left hand side) and 6 (right hand side)

of the archaeological analysis of the wall plug built for closing the loggia. This masonry, in fact, is dated between the beginning of 16th century and the beginning of 17th century AD by the mensio-chronology of bricks (samples 9 and 17), the radiocarbon dating of lump n.6 and the results of the mortar analysis. Result of the thermoluminescence dating of the brick is consistent with the results of the radiocarbon dating of the lumps n.8 and 12a and with result of the mensio-chronology dating of some bricks found in the SU 17. These results suggest a contamination of the material used to build the loggia with more old building materials. The lump n.6, instead, can be considered a contamination of the "original" material due the remains of a render built a few centuries after the loggia and removed before the analysis.

These two cases of contamination highlight the sampling problems in archaeological researches that can seriously affect the result of the whole study, According to the described experience, the most common contaminations originate from due causes: the size of the samples that are collected and the recognisability of the building materials belonging to different phases.

Size of the samples. This cause was highlighted by the mortar analysis carried out for the characterization of the aggregate and due to the tiny differences in the sand used to date the mortars. The differences among the sands that characterize the beaches of Genoa, in fact, sometimes are very subtle. In some cases, for instance, the difference is not in the petrographical composition but in the relative ratio of minerals. All the sands coming from the sectors 3, 4 and 5 located nearby the port are made of quartz, marl limestone and ophiolites but, compared each other, show a different relative ratio of these minerals. The sand from "Ripa", in fact, is mainly made of quartz and contains a small amount of marl limestone and ophiolites. The sand from "Fassolo" (sector 4), instead, is mainly made of quartz and marl limestone with very few ophiolites. Sampierarena's sand, finally, is mainly made of ophiolites with a small amount of quartz and marl limestone.

These small differences entail the constant need to collect reasonable big pieces of mortar, if possible with a quite broad range of grain size in order to avoid the sand segregation problem. This problem is mainly due to the different density of grains as well as the different hardness of the minerals.

The minerals, in fact are represented differently in the different fractions of the sand, from the finer to the coarser. Harder minerals such as the quartz, for instance, are found in all the fractions while the limestone is mainly represented in the coarser fractions. This means that if a fraction is not represented in the sample, the result of the petrographic analysis can be different. In the case of the façade located in Vico delle Fate, a first sampling activity lead the geologist to recognize sand from the Sampierdarena beach in the most part of the samples. However, a more accurate analysis of the façade, suggested collection of new bigger samples that changed the initial results. The new analysis, in fact, suggested that the sand of the mortars collected in the loggia is from a small beach close to the city centre (sector 3/5) whose composition is mainly made of quartz and ophiolites and is comparable to a mix of the RIpa's sand and the Sampierdarena's sand. This sand has been rarely found in other archaeological researches [Ricci, 1988, 47] but is believed to have been used during the late middle age. This result changed the chronological information about the loggia obtained with the initial mortar analysis. The new data, in particular, shifted the supposed age of the mortars toward a previous period that matches better the other archaeometric data, including the results of the radiocarbon dating of lime lumps collected in the same mortars.

Recognisability of building materials belonging to different phases. The lump n.6 previously discussed is a clear example of contamination, recognized only by an uncommon analysis: the radiocarbon dating of mortars. This contamination, in fact, could not be recognized during the sampling work (fig.1), neither during the analysis with the optical microscope and only after having received the results of the radiocarbon dating it has been possible to identify a more recent layer of mortar on the masonry where the lump was sampled.

Only at this stage, in fact, it has been possible to understand that the remains of a render no more existing at the time of the analysis filled a gap in an older mortar used to bind the bricks. Obviously, demolition of the render did no remove completely its traces that are hardly recognizable still now. Composition of both, contaminant and original material, in fact, are very similar: the same air lime and the same sand made of quartz, marly limestone and ophiolites, without additives and/or additions that could be used to distinguish between the two mixes. Usually, in such a case the only possible way for identifying the contamination is by following the borders of the remains but, as already said, this was a very small piece of render in a gap within of a very similar mortar and the borders between the two materials are almost completely invisible[9].

Overall, it is quite obvious that any sample collection must be carried out only after a very careful observation of the structure where the samples have to be taken. Nevertheless in some cases the interfaces among the different layers are not clear and the materials are very similar. As this research shows, a high number of data (i.e. samples, dating) allows the recognition of the errors but unfortunately the collection of such a high number of information is not always possible. This force the researchers to pay the utmost attention during the sampling work and force them to verify systematically all the obtained results. Otherwise the result of all archaeological analysis can be affected.

6. Conclusions

The choice of a structure with numerous and easily datable features for carrying out a test on the accuracy and precision of the "pure lime lumps" technique allowed highlighting the good consistency of the results achievable with this technique (e.g. results of the lumps 2, 4, 5 and 7) and the good consistency of the results obtained with different dating methods such as the radiocarbon dating of mortars, the mensio-chronology of bricks and the chrono-typology or mortars.

The complexity of the façade, though, highlighted also some limitations of the practical work that can have huge effects of the final results of the analysis. Some of these limitation have been discussed in this contribute together with their causes and the available solutions.

Notes

Paragraphs 2, 3 and 5 of this paper have been written by R. Vecchiattini and paragraphs 1, 4 and 6 by G.L. Pesce.

[1] Precipitation of calcium carbonate contained in the limestones, in fact, took place far back in time compared to the half-life of the 14C. For this reason these materials do not contain 14C and are said as: "14C-dead".

[2] Research project of Athenaeum 2011 (funded in January 2012): "Evaluation of the potentiality and limitations of the radiocarbon dating method (14C) applied to the lime mortar used in historic buildings". Scientific responsible: arch. Rita Vecchiattini. The project was funded again the following year (January 2013), with the title: "Evaluation of the potentiality and limitations of the radiocarbon dating method (14C) applied to the lime mortar used in historic buildings - second part".

[3] The mensio-chronology of bricks is an absolute dating method valid only at local scale. The method is based on the connection between the measures of the bricks (in particular, length and thickness; "mensio" means "measure" in Latin) and their production time. This connection has already been demonstrated in several Italian cities [Mannoni e Milanese, 1988; Ghislanzoni e Pittaluga 1989; Ghislanzoni e Pittaluga 1991, Pittaluga, 2009]. Researches carried out in Genoa, highlighted a constant reduction of the size of the bricks since the medieval age until the 18th century that is believed to be due to an economical reason. In the past, in fact, the bricks were sold by number and not by weight and this made much more advantageous for the producer to reduce the size of the bricks rather than keep their dimensions constant. With smaller bricks, in fact, a wall had to be built with more elements and the profit for the producer could be higher. The reduction, however, was illicit because strict laws ruled this type of production in order to guarantee the safety of the constructions. Consequently, the reduction could not be too obvious. Inspections at the productive sites were quite common and the sanctions high. This strict control caused a small but continuous reduction in the size of the bricks that can be used today for evaluating the time of production. Studies carried out in Genoa and confirmed later by researches in other Italian cities, promoted the development of conversion curves where the size of the bricks is clearly related to its time (mensio-chronology curves). Of course, each administrative unit has its own curve that cannot be used in other cities. For this reason this method, despite the fact that is an absolute dating method, is valid only on a local scale.

[4] The chrono-typology of mortars is an absolute dating method valid only in Genoa and based on the connection between the composition of the aggregate contained in the mortars and the time when these mixtures were prepared [Mannoni, 1982; Ricci,

1989; Ricci, 1998]. The method is based on two factors: 1) places where the sand was extracted (mainly beaches) changed during the time following the expansion of the urban area; 2) mineralogical composition of the sands around Genoa is different because the geological characteristics of the mountains around the city. Combination of these two factors allows to date the mortars by analysing the mineralogical and petrographical composition of the aggregate. By knowing the time when a particular sand was used, in fact, it is possible to date the mixes where the sand was used. For instance, researches already showed that the sand from the beach of the so called "Ripa", could had been used only between the 11th and the 14th century AD, while the sand from the beach of Sampierdarena has been intensively used between the 15th and the 19th century. Consequently, mortars containing these two types of sand could had been mixed only in the respective period of time, This method has been used in Genoa for decades with consistent results and cannot be used in other places, unless similar natural conditions are available. The uncertainty in the result of the dating method is quite variable and can also be quite wide (e.g. the case of the sand from Sampierdarena) but the results from this dating method can still be useful in archaeological researches where stratigraphic information are only few or not clear and more chronological information are needed.

[5] The "Genio Civile" is a peripheral government body instituted in 1882 for monitoring, tracking and with the role of superintendence on public works, at peripheral and local level.

[6] The analyses were carried out by arch. Daniela Pittaluga and arch. Rita Vecchiattini of the Department of Science for Architecture of the Scuola Politecnica of Genoa.

[7] The radiocarbon dating of lumps was carried out at the Centre for Dating and Diagnostic of the University of Salento (Lecce, Italy). Director: Prof. Lucio Calcagnile.

[8] The thermoluminescence dating was carried out by Dr. Emanuela Sibilia at the Laboratory of Archaeometry of the Department of Material Science - University of Milano Bicocca, Milan (Italy).

[9] Very narrow cracks can be noted in the mortar around the sampling point of the lump, and this could testify the demolition of the render. This work, in fact, was usually carried out using hammer and chisel and this traumatic action could have produced the above mentioned cracks.

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