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Radiocarbon Dating of Lumps of not Completely Mixed Lime Contained in Old Constructions: the Sampling Problem

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Abstract This paper deals with the technical and methodological sampling problems of lumps of not completely mixed lime putty in mixtures, in order to obtain a suitable material for the radiocarbon dating of mortars and plasters. Sampling of this type of lumps, in fact, allows us to be able to use a suitable material for the radiocarbon dating of lime mixtures (e.g. mortars, plasters, lime bed of mosaics, frescos paintings, etc.) because in this way it is possible to avoid the contamination problems deriving from sources of carbon such as the "14C-dead" of limestone sand or of not completely burned limestone. From an archaeological point of view, this sampling procedure gives the possibility to obtain an accurate radiocarbon dating for each piece of masonry considered without any considerable damage.

1 Introduction

Mortars have been exploited as material for radiocarbon dating for a long time [1-7]. The basic principle of the method is quite simple: lime is produced from limestone (essentially CaCO₃, calcium carbonate) of geological origin ("dead" in terms of radiocarbon concentration) which, in the past, was burnt at about 1173 K to produce CaO (quicklime). Lime was used, for example, for mortars and render, by slaking quicklime with water and mixing this slaked lime with sand (aggregates). When in place, these mixtures (essentially formed by Ca(OH)₂ + aggregates) harden by absorbing CO₂ from the atmosphere and becoming again calcium carbonate (Ca(OH)₂ + CO₂ → CaCO₃ + H₂O). As a result of this process, the calcium carbonate contained in the mortar reflects the atmospheric ¹⁴C concentration at the time of hardening and thus, this material can be used for radiocarbon dating.
Despite the fact that this method may be very simple in its principles, several studies have shown its drawbacks and limitations [8] which are mainly due to the contamination of the samples from carbonaceous substances such as pieces of incompletely burnt limestone containing “$^{14}$C-dead” and aggregates of fossil origin (e.g. limestone sand).

Furthermore, although more recent studies have shown that accurate sample processing treatments allow the significant reduction of these error sources [6], a new, different sampling procedure based on the selection of lumps of incompletely mixed lime, often visible in the mixtures, is a very interesting alternative for the absolute dating of lime that does not deal with the problems of contamination. This method was demonstrated by the author in a paper published in the Radiocarbon journal [9]. The correct selection of lime lumps carried out with the aid of an optical stereo microscope, allows pure lime samples reflecting the atmospheric $^{14}$C concentration of the time of the mixture hardening to be obtained, without doubts of contamination problems deriving from any sources of old $^{14}$C”.

2 The case history and the main characteristics of the lime lump sampling and dating method

Since 2007 we have applied this sampling and dating method to 11 samples of lime lumps coming from four different buildings: the Medieval church of S. Nicolò of Capodimonte (Camogli, Genoa – Italy; [9]); the Medieval Crypt of the Reggio Emilia Cathedral (Reggio Emilia - Italy); the Medieval Castle of Zuccarello (Zuccarello, Savona - Italy) and the Medieval Castle of Donnetta (Torriglia, Genoa - Italy). The above mentioned samples were the only samples picked up in these buildings and for each sample we obtained results that perfectly met the dating obtained by other archaeological methods.

In the same manner some years ago other researchers carried out radiocarbon dating of lime lumps on the alto-Medieval castle of Aghinolfi (Massa Carrara – Italy; [10]) and on the basilica of S. Lorenzo Maggiore in Milan (Milan – Italy; [11]) which have had a very important role in the comprehension of the history of these two buildings.

This case history provides evidence of the importance of this sampling and dating method in the field of archaeology. In fact, this method has some very suitable characteristics for the majority of archaeological research carried on in both the field of excavations and in the field of building archaeology. Radiocarbon dating can be done with a very small quantity of lime (20 milligrams) if Accelerator Mass Spectrometry is used: this quantity is perfectly comparable with the dimensions of a single lime lump obtainable from the majority of aerial lime mixtures we have studied. This means that each time the work necessary to obtain a suitable sample of lime for a radiocarbon dating involves the destruction of a
very small part of the object (this does not always happen with other dating methods).

Besides, the cost of a single dating is not so expensive as the other dating methods (e.g. thermoluminescence), and these items are more and more important if we compare this cost with the typical budget of archaeological research.

Furthermore, thanks to the fact that reused pieces of masonry containing mortars or plasters can be easily recognised, it is possible to avoid the problem of the dating of reused materials as, instead, happens with some other materials like brick, when the thermoluminescence method is applied to some samples of reused material.

However, not all the characteristics of this sampling and dating method match all the needs of archaeologists and, as happens with other dating methods, this method has some application problems. In fact, some issues are still to be addressed such as the quite large calendar time ranges resulting from the calibration of the conventional radiocarbon ages, that often make the results not so useful to resolve archaeological problems. This problem is strictly related to the shape of the calibration curve in the studied temporal range which is not discussed here. Nevertheless, in this circumstance we can underline that the application of advanced statistical tools, such as Bayesian based methods, to constraint radiocarbon determination with stratigraphic or historical information can be expected to be a fundamental help to reduce the calendar time ranges [9]. The main objective of this paper is to underline the problems connected to the sampling method of the lime lumps for the radiocarbon dating.

3 The sampling method of lumps of lime putty for radiocarbon dating

The above mentioned dating, developed in recent years by different research groups, shows that the dating of lumps of incompletely mixed lime is a very promising method to obtain absolute and direct dating mortars, plasters, renders, mosaic substrate, frescos paintings, etc.

However, at the same time, these cases show that the method relies on the correct sampling of lime lumps (it is for this reason, that in the previous paragraphs this method has been called: “sampling and dating method”). Thus, in order to clarify, as best as possible, the work necessary to achieve the correct results, it is necessary to concentrate our attention to the sampling method and in doing this, it is necessary to consider the problems in two sectors: the problems related to the on site sampling and the problems related to the identification of lumps of pure lime which are not mixed.
3.1 Problems related to the on site sampling of lime lumps

The first thing to consider is the condition of the structure (building out of the ground, underground walls, frescos layers, mosaic substrate, etc.).

If we work in the field of building archaeology, in which we can’t often reach the inner part of the walls but only their surfaces, the thickness of mortar joints must be large enough to allow the selection of suitable samples. Basically, this problem depends on the characteristics of masonry that sometimes does not allow a correct lump sampling (this is the case of most parts of the Roman and Medieval constructions made with squared off blocks, laid upon very thin mortar joints).

This problem is less relevant when a wall section is accessible and this happens very often in the archaeological excavations where it is common to find underground masonry.

But if we can reach the inner part of the masonry, another two problems must be considered: the problem of the possible dissolution and re-carbonation cycle of calcium carbonate of lumps due to the water circulation of soil and the problem of the depth of sampling into the wall.

For the first problem, it is necessary to underline that, at present, we have not yet met cases of dating alteration due to this cycle but, sometimes we gave up the sampling work because we had the suspicion that samples could have been affected. This is the case of some Roman mosaics found during the excavation of the crypt of the Reggio Emilia cathedral, where we gave up the radiocarbon dating of lime lumps because we suspected that the increase and decrease of the ground water, that surely involved those mosaics, could affect the results of our samples.
Fig. 1 Mortar joint with lump of lime (upper right corner, inside the red circle)

For the second problem (the depth of sampling into the wall) we must consider that the depth must be sufficient to avoid sampling of mixtures not belonging to the original construction (for example, some plasters applied on the wall after its construction). Furthermore, it must not be too deep to avoid the problem of incompletely carbonated lime lumps or the problem of a delayed carbonation process (with respect to the construction time of the wall). In fact, in some cases, non-carbonated or partially carbonated samples have been found inside the walls.

The carbonation process begins from the external surfaces of the walls and carries on towards the inner parts at a more and more reduced speed. As a consequence of this mechanism, there is the possibility to have samples subjected to a “delayed” carbonation, if we gather samples in the most inner parts of the masonry and this problem should be taken into great consideration during the sampling work.

The mass of a single lump (that must be at least 20 milligrams), has to be evaluated directly in situ in order to have enough material for the radiocarbon dating. If a single lump is not considered to be large enough, it is possible to collect more than one lump. We only need to be very careful in collecting samples from the same part of the masonry that in archaeological terms means from the same stratigraphic unit.
3.2 Problems related to the identification of pure lime lumps

After the on-site sampling and before the radiocarbon dating treatment, it is necessary to check the samples picked up on-site under a stereo optical microscope. This work is necessary in order to verify if the sample is really a pure carbonated slaked lime lump and in order to remove mechanically all the pieces of limestone aggregate pieces that can be attached on the surface of lump.

In order to verify if the sample is a lump really suitable for the radiocarbon dating and not an incompletely $^{14}$C-dead burnt lime (that is a piece of unburned stone, unsuitable for the radiocarbon dating) it is possible to proceed in two ways: by an observation of the lump surface with a magnifying glass and by a very simple test of its hardness.

In fact, often during the on-site work it is possible to find lumps of incompletely $^{14}$C-dead burned lime (pieces of unburned stone) that look like small white and rounded lumps, similar to the lime lump of carbonated slaked lime. But under a magnifying glass, like the glasses of a stereo microscope, even at low magnification (e.g. 10x) it is possible to verify that the surface of lumps of carbonated slaked lime look floury (Fig. 2), instead the surface of uncooked lumps appear to be thick in the manner of a stone.

Besides, if we try to scratch an unburned piece of stone with, for example, a needle point, it is simple to recognize the typical hardness of stones. Instead, if we
try to scratch a lump of carbonated slaked lime, it is possible to observe a softness that sometimes can make it very hard to treat the samples.

Pieces of limestone sand can be removed from the lump surface by using tools, for example, a scalpel. In order to remove as many pieces of sand as possible, this work must be carried out by the use of the above mentioned microscope and must be carried out with great care because it is very easy to damage or destroy the sample because, as we have already said, it is very delicate.

Samples obtained in this way are perfectly suitable for a radiocarbon dating.

4 Conclusion

From the case history we faced it is possible to assert that the radiocarbon dating of lime lumps of carbonated slaked lime is one of the most interesting dating methods for constructions available at present.

In this method the sampling work is one of the most important parts of all the processes that involve archaeological knowledge, chemical and physical knowledge and the knowledge of building materials. In fact, in order to avoid the most elementary dating problems like the dating of hidden repairs, it is necessary to begin the sampling work with a very careful stratigraphic analysis of the object that must be dated (this point is essential to obtain archaeologically correct results) and, after this work, it is necessary to work carefully on the lime lumps both, on site and in the laboratory.

However, the results obtained in recent years are still not enough to allow us to understand completely the potentialities of this method. In fact, some things are still unknown. For example, we must underline that up until now, we have performed dating of lime lumps on samples coming from mixtures containing aerial lime or, at least, feeble hydraulic lime. We have come to know these binders thanks to the theoretical and practical studies that have been performed recently in many parts of the world. But we don’t know exactly what happens in mixtures made with moderately or highly natural hydraulic limes; a type of binder often used in the past. We know, for example, that in mixtures with this type of binder there is always a surplus of calcium hydroxide so that the carbonation reaction is still important, but we don’t know what happens to the lumps. For instance, we don’t know if it is possible to find as many lumps in mixtures made with natural hydraulic limes as in the mixtures with aerial limes and if the presence of silicon dioxide and aluminium oxide in the lime oblige us to discover bigger lumps than the 20 milligram lumps that we sample in the aerial lime mixtures. Or again, if the presence of silicon dioxide and aluminium oxide in the lime can effect the radiocarbon dating.

Thus, in the next few years we must improve our knowledge about these types of binders and, above all, our knowledge regarding their lumps. In doing this, we must consider that, at present, there are only a few articles in the scientific
literature that deal with problems of lime lumps and that these papers do not deal with the problem of their formation processes [12]. Thus, one of the first things that we must understand is exactly what the lime lumps are and how they take form inside the mixtures. Otherwise, we will run the risk of making serious archaeological errors.

5 References