HISTORIC LIME-MORTAR ^{14}C DATING OF SANTA MARÍA LA REAL (ZARAUTZ, NORTHERN SPAIN): EXTRACTION OF SUITABLE GRAIN SIZE FOR RELIABLE ^{14}C DATING

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ABSTRACT. This paper describes a method for effective separation of the pure binder fraction of lime mortars for reliable radiocarbon dating. The methodology allows removal of the detrital carbonate fraction and the unburnt limestone particles, obtaining particles of under 1 μm. The extracted fraction ensured that all carbonate has been generated by slaked lime carbonation. Consequently, the measured carbon corresponds to atmospheric carbon. The proposed method allows to obtain pure datable binder, simplifying considerably the performance of radiometric measurements because dating other grain-size fraction is unnecessary. In order to prove the effectiveness of binder refining, the extraction method has been applied to 5 lime mortars of different archaeological periods from the perimeter walls of Santa María la Real parish church (Zarautz, northern Spain).

INTRODUCTION

Dating ancient buildings and establishing construction phases are important issues for archaeologists and cultural heritage researchers. For radiometric dating, the fundamental requirement is to acquire suitable datable material that records the age of the studied object. Plaster and mortar are composite building materials comprising a mixture of binder and aggregates. Binders in archaeological buildings consist of lime and gypsum, whereas aggregates contain inorganic and organic materials (Sickels 1981). The most common organic component is charcoal, most likely corresponding to residues of the burning process, especially when a continuous wood-fired kiln was used.

Building lime, sand, pottery, and organic materials from mortars have been used previously in dating (Folk and Valastro 1976; Tubbs and Kinder 1990; Heinemeier et al. 1997a, 2010; Schmid 2001; Goedicke 2003; Hale et al. 2003; Benea et al. 2007; Lindroos et al. 2007; Wintle 2008). Organic materials are widely used to date mortar and plaster (Berger 1992; Van Strydonck et al. 1992; Frumkin et al. 2003; Rech et al. 2003; Rech 2004; Wyrwa et al. 2009; Al-Bashaireh and Hodgins 2011) where no other easier datable material is present, such as written inscriptions, coins, and/or historical records (see Heinemeier et al. 1997b, 2010; Hale et al. 2003). Tubbs and Kinder (1990) have reported the unreliability of dating mortar based on organic inclusions because of the old-wood problem. Recently, Heinemeier et al. (2010) presented extensive examples of the same problem and also reached the same conclusion.

The basis of mortar dating can be summarized as follows: limestone (mainly $CaCO_3$) is burned to lime (CaO) and this calcium oxide is then slaked with water to form portlandite ($Ca(OH)_2$). The calcium hydroxide is mixed with aggregates and water to make the building mortar and, during hard-

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ening, the lime mortar absorbs carbon dioxide (CO_2) from the atmosphere to produce calcium carbonate ($CaCO_3$). During the hardening process, the actual ^{14}C concentration of CO_2 in air is fixed to the binder carbonate.

The lime mortar binder represents a potential tool to assess the chronology of the different construction phases of buildings by means of radiocarbon dating. The principle of ^{14}C dating is that binder carbonates absorb carbon dioxide from the atmosphere, thus making mortars potentially suitable for ^{14}C dating. The method of ^{14}C dating mortar has been applied since the 1960s, but frequently the isotopic age and the expected historic age show contradictory results (Labeyrie and Delibrias 1964; Stuiver and Smith 1965; Baxter and Walton 1970; Van Strydonck et al. 1983, 1986, 1992; Ambers 1987; Heinemeier et al. 1997a, 2010; Hiekkanen 1998; Hale et al. 2003; Nawrocka et al. 2005, 2007, 2009; Lindroos et al. 2007; Marzaioli et al. 2011).

In dating building mortars, there are problems in obtaining the correct ages that are related to an adequate binder carbonate selection. Unfortunately, most lime samples contain carbons of different provenances: incompletely burned limestone fragments, charcoal particles from wood-fired kilns, and aggregates (mainly natural sands). Depending on the geological and geographical location, aggregates may also contain carbonate minerals, carbonate rock fragments, and calcareous fossils. In these cases, the aggregates constitute an additional source of contamination in carbon. Therefore, in order to eliminate these error sources, sample preparation procedures have been improved upon since the beginning of the radiometric dating method. Most of these preparations consist of mechanical pretreatment and chemical treatment (Sonninen and Jungner 2001; Lindroos et al. 2007; Nawrocka et al. 2007, 2009; Goslar et al. 2009; Heinemeier et al. 2010).

In mechanical separation, the mortar samples are gently broken and then sieved (different sized meshes are used). Van Strydonck et al. (1992) used a 250-µm sieve, whereas others (Heinemeier et al. 2010 and references therein) utilized an increasingly fine mesh ranging between 20 and 500 µm. Following mechanical separation, the mineral composition is analyzed by petrographic microscopy supplemented with cathodoluminescence in order to identify binder contamination from aggregates and unburnt limestone (Heinemeier et al. 2010 and references therein). In chemical separation, binder carbonate is gradually dissolved by pouring 85% phosphoric acid over the powder mortar under vacuum (Heinemeier et al. 2010), under the assumption that mortar binder carbonate dissolves much more easily than limestone. However, significant amounts of detrital carbonate and other carbon sources are also dissolved, therefore precluding determination of the correct age. Mechanical methods have been used as an alternative to the chemical method for mortars with calcareous aggregates (Cimitan and Zaninetti 1991; Casadio et al. 2005; Nawrocka et al. 2005; Ortega et al. 2008).

Mechanical binder separation is recommended when carbonate contamination has been observed during petrographic analysis. However, gently breaking of the pieces should be avoided because undesirable fine grain-size particles can be produced. In order to obtain the binder fraction, an alternative to gently hammering is a soft manual disaggregation without any mechanical crushing. Therefore, to obtain a pure binder, particle size is critical. Sieving could be the answer, but the lower limit of measurement is considered to be ~38 µm (400 mesh). The fraction smaller than 38-µm size is comprised of particles of both mechanical (aggregates and/or unburned limestone fraction) and chemical (binder fraction) origins, yielding a contaminated fraction (cf. Figure 1b in Lindroos et al. 2007). For smaller particle sizes, sedimentation test methods are recommended (ASTM Standard C33, ASTM International 2003).

In the present contribution, an effective separation method of very pure binder fraction to assess ^{14}C dating is proposed. The elimination of contaminant error sources and a suitable selection of mortar samples enable reliable dating. Petrographic analysis under polarizing light microscopy is used to identify different mineralogical phases of mortar samples, the aggregate nature, and the limestone fragment remains. It also enables identification of possible features of mortar degradation (organic and inorganic) and, therefore, allows the selection of a suitable sample for ^{14}C dating. To obtain datable binder, thin-section assessment is necessary and offers one of the most effective methods for mortar sampling. A more detailed microscopic analysis can be provided by scanning electron microscopy (SEM), which allows contaminant error sources of the mortar sample on a small scale to be identified. Other additional analytical techniques such as particle-size analysis, cathodoluminescence, or thermogravimetric analysis can be of great help and should not be discarded.

Once the aggregate nature and the occurrence of other carbonate materials are established, the binder carbonates are separated by a combined mechanical and physical procedure (Ortega et al. 2008). This method allows removal of the detrital carbonate fraction and the charcoal particles. In order to test the effectiveness of mechanical separation and to verify the purity of the binder, SEM was performed, thus allowing reliable dating without using partial acid digestion and several ^{14}C measurements of complex interpretation. The complete procedure is described in detail below and applied to historic lime mortars from the parish church of Santa María la Real (Zarautz, northern Spain).

ARCHAEOLOGICAL BACKGROUND

The archaeological site of Santa María la Real is located within and surrounding the parish church of the town of Zarautz. The town is located on the Gulf of Biscay, bordering a sandy beach 2 km long. Excavations of the interior of the church of Santa María la Real have identified successive periods of occupation since the Iron Age (Ibáñez Etxeberria 2003, 2009; Ibáñez Etxeberria and Moraza 2005). Remains from the Iron Age and a long-term stable Roman establishment (between the 1st to 5th centuries AD) were located in the room structure uncovered. Within the Roman zone, several room units have been discovered. A new reoccupation of the space by different human groups took place starting in the late 9th century or early 10th century. The evolution of the site is attested through the layout of 4 religious temples and an associated necropolis (Figure 1). Overall, this confirms the foundation and the uninterrupted development of the present-day community of Zarautz from the early and late Medieval periods until the existence of the present temple.

MATERIALS

Five mortar samples of this church were selected for radiometric dating, corresponding to different periods of occupation ranging from Roman (1st–4th centuries AD) to Medieval (9th–14th centuries) periods (Table 1). Before dating, the selected mortar samples were subjected to petrographic analyses in order to determine binder and aggregate types. Thin-section analysis shows that beach sand aggregates were used as a mortar mixture. Rounded to subangular detrital quartz grains, sandstone fragments, and carbonate shell fragments (mainly ostracods) are the main components of the aggregates (Figure 2). Although the geological environment is mainly comprised of calcareous sedimentary rocks, within the aggregate fraction inorganic detrital carbonate fragments (micritic and/or sparitic limestone) are scarce (Ortega et al. 2008). However, petrographical differences related to the ratio binder/aggregate and sorting grade of the aggregate particles occurs and can be associated with the archaeological period of mortars. Two main types of frameworks were distinguished according to the amount of sand present. Roman mortars show an open framework with detrital grains dispersed in the binder and a low sorting grade of aggregates (Figure 2a). The aggregate grain size
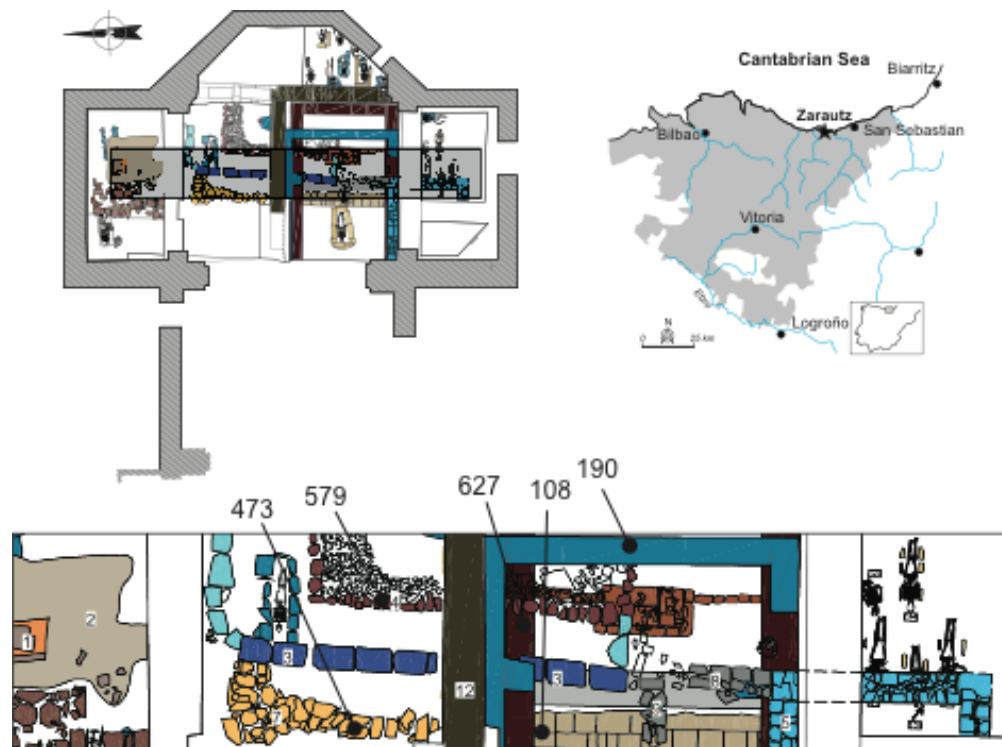
Figure 1 Scheme of the studied church showing the setting of different epoch structures and the location of mortar samples: 1–2: Iron Age structures; 3–9: Roman epoch structures; 10–11: Temple I; 12–13: Temple II; 14–15: Temple III.

ranges from 0.3–0.5 mm for quartz and carbonate shell fragments, and up to 3 mm for limestone rock fragments. Meanwhile, the early Medieval mortars corresponding to temple I show a close framework and poorly sorted aggregates (Figure 2b). Temple II Medieval mortars also show a close framework of well-sorted aggregates (Figure 2c). Temple III mortars have an open framework with a high sorting grade of aggregates (Figure 2d).

Pure carbonate lumps of macroscopic and microscopic scale are common in all mortars (Figure 2f), suggesting an inhomogeneous mixture of carbonate binder and aggregates (Nawrocka et al. 2005; Ortega et al. 2008). Rarely within carbonate lumps unburned limestone fragments are observed and most of them occur in Roman mortars (Figure 2d). Moreover, differing chemical compositions of the binder have been reported previously based on their archaeological period (Ortega et al. 2008). This suggests different provenances for the limestone used in quicklime production.

METHODS

The protocol established to obtain pure datable binder is based on a modification of the procedure described by Sonninen and Jungner (2001), widely used in the ^{14}C dating of mortar (Nawrocka et al. 2005, 2007, 2009; Lindroos et al. 2007; Goslar et al. 2009; Heinemeier et al. 2010). The mortar samples were gently crumbled by hand and, based on the assumption that binder carbonates are characterized by an easily breakable aggregation structure, they were disaggregated by means of an ultrasonic bath.
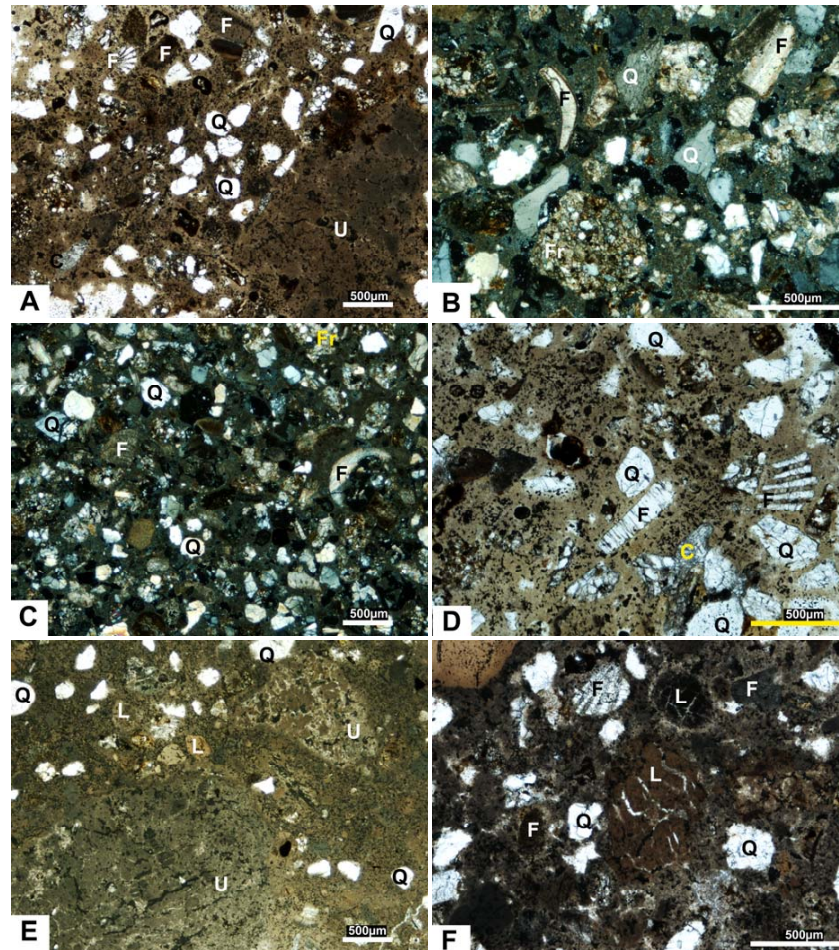
Figure 2 Photomicrographs of historic lime mortars: A) Roman mortar shows an open framework with poorly sorted detrital grains within the binder; B) Medieval Temple I mortar with a close framework and poorly sorted aggregates; C) Medieval Temple II mortar with a close framework of well-sorted aggregates; D) Medieval Temple III mortar with an open framework of well-sorted aggregates. The aggregates' main constituents are rounded/subangular quartz, sandstones, and carbonate shell fragments; E) soft, rounded for unburnt limestone; F) carbonate "pure" binder lump showing fractures. Abbreviations: Q: quartz; U: unburnt limestone; F: fossil remains; Fr: rock fragment; C: carbonate (esparitic calcite); L: lump.

Our method is based on the fact that particle size is related to mechanical or chemical origin. Geological particles of mechanical origin have a grain size >1 μm, whereas chemical reactions produce colloids that flocculate and regrow, generating finer particles. This fact has been demonstrated for subaerial media (Wilson and Spengler 1996; Seinfeld and Pandis 2006) and for aqueous media (Davis and Kent 1990; Salama and Wilson 2000).

In order to validate this assumption, experimental limestone grinding has been performed using a Retch Vibratory disc mill RS 100 (Retsch GmbH, Haan, Germany). To assess the particle size obtained, a Mastersizer 2000 particle analyzer (Malvern Instruments Ltd, Malvern, UK) was used to measure grain size. A particle distribution histogram shows an unimodal distribution ranging from

0.4 to 20 µm (Figure 3A). Observations by electron microscopy of the surface morphology of these grains show angular, freshly crushed shapes characteristic of their mechanical origin (Figure 4A).
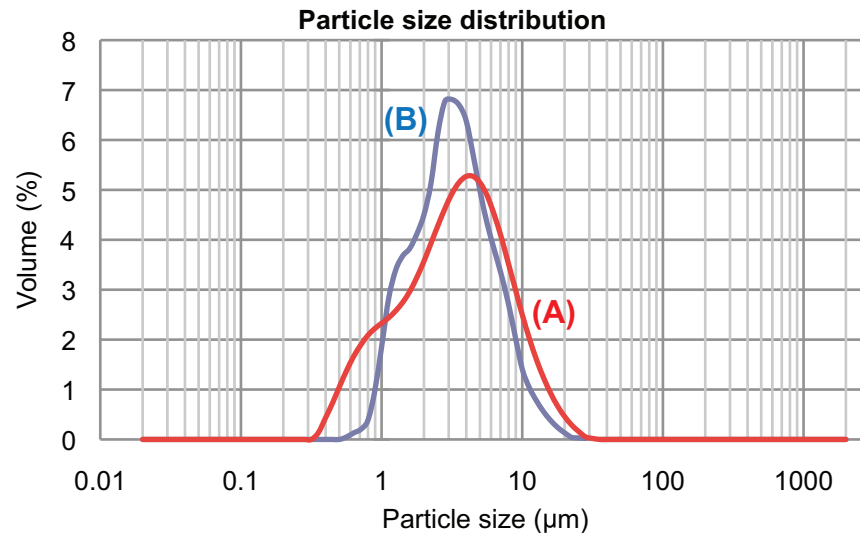

Figure 3 Grain-size histograms for particles of experimental limestone grinding: A) particle distribution of the whole fraction; B) particle distribution after 12 hr submerged in water (pH 5–6).
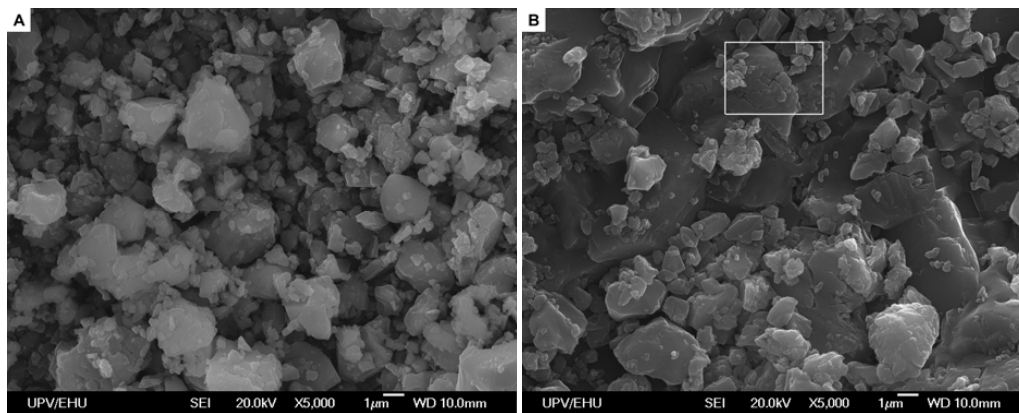

Figure 4 SEM photomicrographs: A) limestone whole fraction where grains with angular, freshly crushed shapes are observed; B) remaining particles after 12 hr sank in water with the absence of the finest fraction.

The grinding results contradict the geological detrital sediment and clastic rock studies as well as the experimental simulations of particle-size productions during geological processes (Wright 1995; Wright et al. 1998; Smalley et al. 2005). The absence of finer grain-size fraction in geological materials is the result of weathering and transport processes in aqueous media. A series of laboratory simulations was set up reproducing weathering and transport conditions to demonstrate that grain-size fractions <1 µm are quickly dissolved in natural waters (pH 5–6) after a short period of time. After 12 hr, the ground whole limestone sunk into simulated natural water and all the finest fraction was dissolved (Figure 4B). A particle distribution histogram shows an unimodal distribution with a mode at 4 µm, a shoulder at 1.5 µm, and a small tail up 20 µm (Figure 3B). Most of the particles

<1 μm disappear, and also the mode shifts from 4 to 3 μm. This mode shifting is a result of water acidic dissolution. Not only were the finest particles dissolved, but also coarse grains show signs of partial dissolution (Figure 5). Therefore, particles <1 μm must be produced by crystal nucleation and growth. Several experimental studies simulating mortar production show that binder carbonates are characterized by 200–400 nm fine-grain size (Genestar and Pons 2003; Stefanidou and Papa-yianni 2005; Marzaioli et al. 2011) due to the high hardening rates of lime mortar (Moropoulou et al. 2000; Lanas et al. 2004; El-Turki et al. 2007; Kosednar-Legenstein et al. 2008). The rather high rate of carbonation leads to the isolation of the atmospheric $^{14}CO_2$ signal absorbed by the mortars during their setting. Therefore, our work has optimized a procedure to obtain particles of <300 nm, which ensures that all the carbonate separated has been generated by slaked lime carbonation, and consequently, that the carbon we are measuring corresponds to atmospheric carbon.
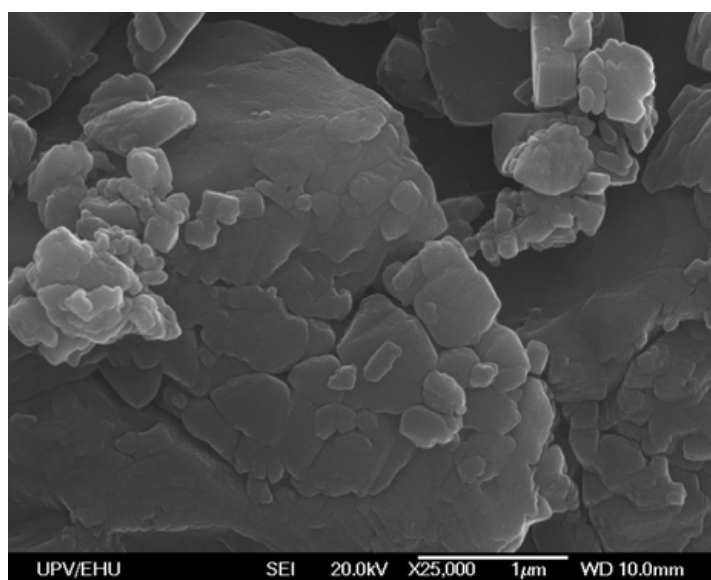

Figure 5 Detail of Figure 4B SEM photomicrographs showing partial dissolution of coarse grains.

The proposed methodology is a variation of the particle-fractionation techniques routinely used in soil and clay mineralogy studies. Sedimentation and centrifugation allow the routine separation of particles <2 μm (Laird and Dowdy 1994; Soukup et al. 2008). Particle fractionation is based on the differential settling of particles in a liquid, so that centrifugation increases the rate of sedimentation, accelerating the process. The relation between the sedimentation rate and particle size is given by Stokes' Law (Stokes 1851):

$$V = g(s_p \sim s_l)D^2/1.8h$$

where V is the particle velocity (cm s^{-1}) in the liquid of density (s_l); g is the gravity acceleration (9.8 cm s^{-2}); s_p is the particle density (g cm^{-3}); D is the equivalent spherical diameter of the particle (cm); and h is the viscosity of the liquid (Pa s).

The main goal of this separation procedure is to avoid (or minimize) the aggregation of small particles and to fractionate particles <1 μm. The procedure has been designed in different particle-fractionation steps as follows:

1. The manually crumbled mortar is placed in an ultrasonic bath with 150 mL of ultrapure water at pH 8 for 10 min to promote further crumbling.
2. The topmost 50 mL by volume is collected from the suspended fraction and corresponds to a particle size of <20 μm. Figure 3A shows a particle distribution histogram with 2 modes, one for fine particle size (0.2 μm) and the other for coarse (~1.5 μm), with a tail reaching 20 μm.
3. To improve the grain-size separation of this <20-μm fraction, it is resuspended in 65 mL of aqueous medium and, once again, is placed in the ultrasonic bath to promote particle disaggregation. The pH 8 aqueous medium favors optimal scattering of small crystals (Warkentin and Maeda 1980) and precludes any partial dissolution of binder particles. This suspension is centrifuged for 60 s at 1000 rpm, using a Kubota 3000 centrifuge (Kubota Corp., Tokyo, Japan).
4. The uppermost 15 mL are collected, which corresponds to a grain-size fraction of <1 μm and a mode of 200 nm (Figures 6A and 7).
5. This fraction is purified via centrifugation at 3000 rpm for 10 min. This procedure is repeated as necessary to obtain a sufficient amount for accelerator mass spectrometry (AMS) analysis. In this study, this process had to be repeated 5 to 8 times to obtain 40 to 80 mg of sample.
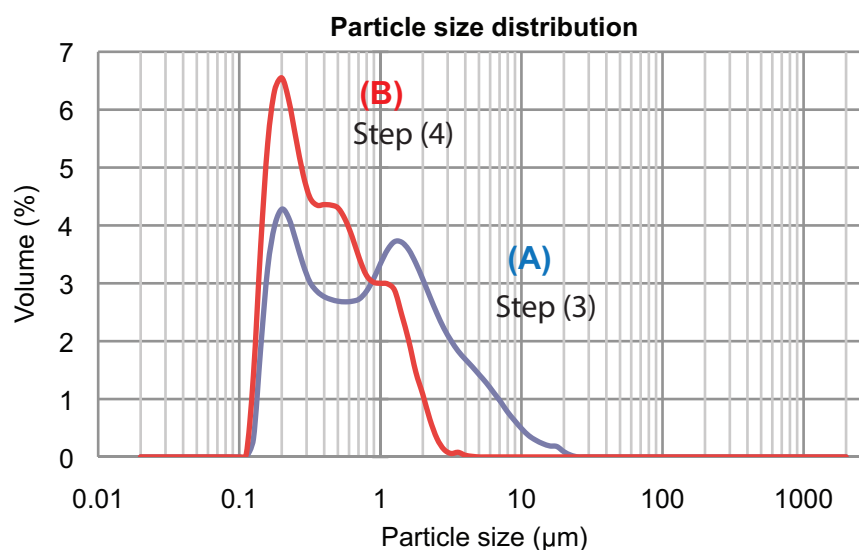

Figure 6 Grain-size histograms for particles extracted from Roman mortar (sample SNR-579): A) The distribution after extraction step 3 exhibits bimodality with a large number of particles in a mode at small sizes (0.2 μm) and coarse size mode (1.5 μm) and with a tail reaching to 20 μm; B) The distribution after extraction step 4 shows a mode at 0.2 μm and 2 shoulders at 0.5 and 1 μm with a little tail reaching to 4 μm.

By means of this procedure, the carbonate binder particles (formed through the reaction of the lime with atmospheric carbon) separate from the detrital and/or fragmented particles. In this way, any supply of dead or nonatmospheric carbon is removed. The separation of the carbonate binder can be confirmed by electron microscopy. Figure 7A shows planar crystalline carbonate grains with a grain size of ~0.2 μm. The coarse fraction discarded can be seen in Figure 7B. This fraction commonly contains particles with a grain size >1 μm and exhibits freshly crushed shapes derived from their detrital origin.
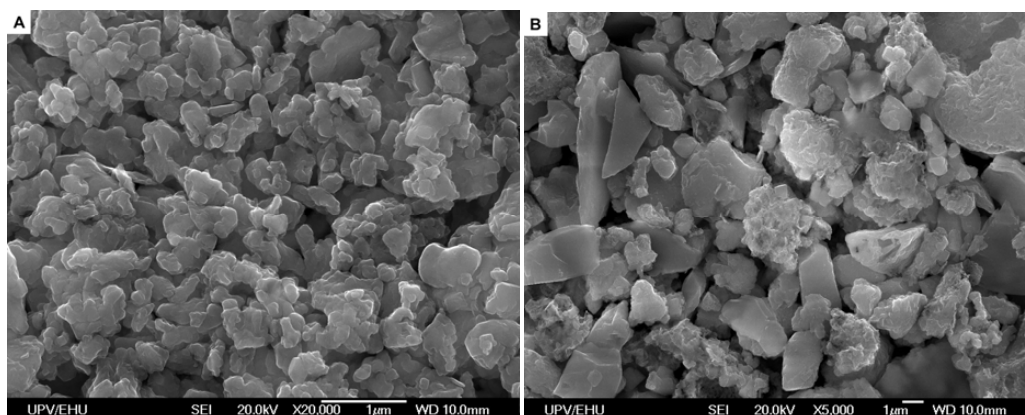
Figure 7 SEM photomicrographs of extracted carbonate from mortar samples: A) fine fraction of sample SNR-108 with minute carbonate grains (average particle size ~0.2 µm); B) coarse fraction of sample SNR-108 with detrital or mechanically fragmented inherited carbonates (particle size <2 µm) showing splintery fractures.

RESULTS AND DISCUSSION

Since Folk and Valastro (1979) evaluated the lime mortar absolute chronology by means of ^{14}C, their results remain uncertain. Several studies tried to isolate the atmospheric $^{14}CO_2$ signal absorbed by the mortars (in the binder fraction) during their hardening. The main problem consists of suppressing the fossil carbon contamination resulting from the incomplete burning of the limestone during quick lime production, and/or the occurrence of carbonate nature aggregates that provide biased dating for historical mortars.

Mechanical binder separation is recommended when carbonate contamination is expected, since during chemical sequential dissolution significant amounts of detrital carbonate and unburned limestones are also dissolved, precluding the correct age determination. To obtain binder fraction particles (i.e. grain size <1 µm), the most suitable method is an extraction procedure by sedimentation. The extraction of the finer fraction allows removal of particles with angular and freshly crushed shapes indicative of mechanical origin and unburned limestone remains. The sieving procedure applied to refine the mortar (e.g. Heinemeier et al. 1997a; Lindroos et al. 2007; Nawrocka et al. 2007; Goslar et al. 2009; Heinemeier et al. 2010) is not useful because smaller grain-size particles extracted correspond to a mixture of binder and detrital aggregates including unburned limestone particles. Moreover, SEM analysis must be performed to verify the morphology of particles in order to ensure the absence of binder contamination.

The extraction procedure developed here is useful not only for mortar with carbonate-bearing aggregates, but also must be applied regularly to ensure that also unburnt limestone particles have been removed. The unburnt problem and its contribution to bias in age determination has been studied by Marzaioli et al. (2011).

The extraction method has been applied to obtain binder for ^{14}C dating of the lime mortars from Santa María la Real church (Zarautz, Spain). The data revealed the age of various construction phases (Table 1). The earliest age determined ranges between AD 90–210 (with 95.4% probability) and corresponds to construction phases at the end of the 1st or 2nd centuries AD (Figure 8). This age is in agreement with the relative timeline indicated by the abundance of common early Roman pottery and with the remains of Hispanic *terra sigillata* pottery found at the site (Ceberio 2009; Cepeda

Ocampo 2009; Esteban Delgado et al. 2012). The oldest remains of Hispanic *terra sigillata* pottery correspond to pottery produced at Tritium Magallum from AD 40 to 60, equivalent to the earliest age of foundations for the Roman structures. In fact, the fill of a foundation trench for the main structure preserved from the Roman period contained fragments of Hispanic *terra sigillata* pottery (Cepeda Ocampo 2009) and of common hand-made pottery (Ceberio 2009), as well as a charcoal fragment in the mortar. This carbon fragment was dated by ^{14}C to 1930 ± 40 BP (Ua-20919), corresponding to a calibrated age of 40 BC to AD 140 with 95.4% probability (Ibañez Etxeberria and Sarasola Etxegoien 2009). These ages are perfectly consistent since, in ^{14}C dating calibration, one has to take into account the problem of old wood (Bowman 1990). Wood or carbon fragments in a mortar are always older than the mortar itself. The difference can be significant if the carbon analyzed derives from the internal part of the tree trunk used as fuel to produce the mortar, or even more so if the wood comes from trees cut long before.

Table 1 AMS ^{14}C dates for mortar samples.

| Lab code	Sample	Conventional age	δ^{13}C (‰)	Calibrated age	Archaeological period
Beta-300900	SNR-579	1860 ± 30 BP	−9.4	AD 90–214 (68.2%) AD 80–231 (95.4%)	Roman
Beta-300899	SNR-437	1870 ± 30 BP	−10.5	AD 92–210 (68.2%) AD 73–227 (95.4%)	Roman
Beta-300898	SNR-190	1220 ± 30 BP	−17.3	AD 729–870 (68.2%) AD 692–888 (95.4%)	Temple I
Beta-300901	SNR-627	1100 ± 30 BP	−17.4	AD 897–985 (68.2%) AD 887–1014 (95.4%)	Temple II
Beta-300897	SNR-108	1060 ± 30 BP	−11.8	AD 905–1019 (68.2%) AD 896–920, AD 950–1024 (95.4%)	Temple III
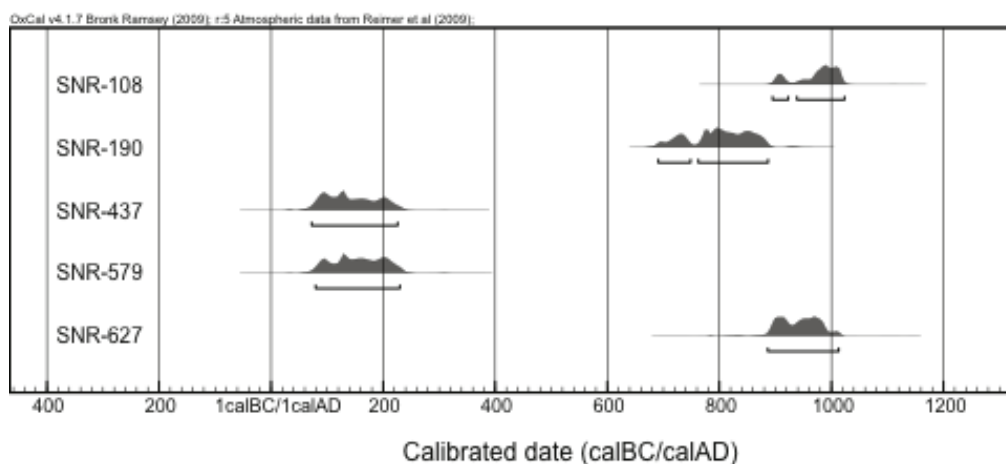
Figure 8 Calibration (2 σ) of ^{14}C dates of the Santa María la Real mortar samples, obtained with OxCal v 4.1.7 (Bronk Ramsey 2009) and IntCal09 atmospheric data (Reimer et al. 2009).

This date belongs to the earliest years of Roman occupation on the northern coast of Spain, associated with the creation of coastal sites for maritime trade occurring in the second half of the 1st cen-

tury AD (Fernández Ochoa and Morillo Cerdán 1994; Esteban Delgado 2004). In contrast, despite the persistence of this settlement for various centuries during the Roman period, as shown by the finding of Late Empire coins and common pottery (3rd–5th centuries) (Cepeda Ocampo 2009; Esteban Delgado et al. 2012), no significant later structures have been dated. The main reason is that, at this site, the later buildings documented are of poorer construction, with walls mortared with mud (Ibañez Etxeberria 2009).

For the Medieval period, the dates obtained correspond to the construction of the perimeter walls for various buildings of the parish church. These buildings are built one atop the other on the same religious site (Figure 1) due to greater need for space as a result of population growth in Zarautz in the Early Medieval period. The oldest age, consistent with the archaeological findings, is provided by the mortar in wall SNR-190 (Temple I), with a probable age of AD 772 to 870 (68.2% confidence interval). This date is close to that established by archaeological analyses for an arch of Temple I, and therefore is not likely a spurious date. Slightly older ages were obtained in skeletons from burials associated with Temple I. Thus, the skeleton sample Ua-16897 provides an imprecise age of AD 558 to 870 (95% confidence interval), and probably prior to AD 770 (68.2%) (Ibañez Etxeberria and Sarasola Etxegoien 2009).

The other 2 ages belong to the perimeter walls of temples II and III. The age for Temple II must be prior to AD 985 (68.2%), whereas Temple III provides an age of AD 970–1020 (95%). These 2 construction phases give ages very close to each other, which are consistent with the population surge at the end of the turn of the millennium and the subsequent need for a larger temple.

The ages determined are coherent not only with the archaeological information, but also with previous radiometric datings. The age for Temple II is very close to that determined for the burials in stone-slab graves in the necropolis, dated to AD 890 to 1040 (68%), whereas individuals associated with the Temple III necropolis, with walled graves, give ages of AD 990 to 1160 (Ibáñez Etxeberria 2003).

CONCLUSIONS

A new procedure for extracting particles of <1 μm was successfully applied to obtain suitable datable binder of lime mortars. The method enables removing the fossil carbon contamination from unburned limestone residuals and carbonating nature aggregates. SEM analysis verifies the particle morphology to ensure the absence of binder contamination. The binder fraction shows a crystalline habit, while undesirable particles are freshly crushed for detrital grains and soft rounded for unburned limestone. The extraction procedure should be applied regularly to ensure removing unburned limestone particles even in the absence of carbonate-bearing aggregates.

The preparation method was successfully applied to 5 lime mortars of different archaeological periods. Samples correspond to the perimeter walls of different buildings within Santa María la Real church in Zarautz. The radiometric ages of the studied mortars are consistent with the age established by archaeological studies for different construction phases of the studied church.

The procedure of binder refining simplifies considerably the performance of radiometric measurements because the binder isolates the atmospheric $^{14}CO_2$ signal during mortar hardening. Therefore, dating other grain-size fractions is unnecessary because they are constituted by a mixture of different carbonates (binder, unburned limestones, and carbonate aggregates).

ACKNOWLEDGMENTS

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