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## **<sup>14</sup>C MORTAR DATING: THE CASE OF THE MEDIEVAL SHAYZAR CITADEL, SYRIA**

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**ABSTRACT.** This paper reports the results from applying the Cryo2SoniC (Cryobreaking, Sonication, Centrifugation) protocol to some lime mortars sampled from the citadel of Shayzar (Syria). The overall aims of this project are 1) to use the properties offered by high-precision accelerator mass spectrometry (AMS) radiocarbon dating for the evaluation of absolute chronology with its typical robust time constraints (i.e. 25 <sup>14</sup>C yr), and 2) to apply the dating directly to the citadel structures in order to prevent possible biasing effects potentially affecting indirect <sup>14</sup>C dating on organic materials found at the study site. The analyses presented in this paper have been mainly performed as a preliminary check of the Cryo2SoniC methodology in order to assess its applicability to this study site by comparing observed mortar results with archaeological expectations about the citadel development phasing and charcoals found encased in mortars. Petrographic and mineralogical thin-section analyses by optical microscopy (TSOM), X-ray powder diffraction (XRD), and scanning electron microscopy plus energy dispersive spectroscopy (SEM/EDS) investigations were carried out for characterization of the mortar samples to verify the occurrence of some features, related to their production technology, which may introduce dating offsets. The resulting <sup>14</sup>C calibrated ages were in agreement with the archaeological expectations based on type and stratigraphic site reconstructions, *in situ* inscriptions, and written sources. Such results showed also a general (with 1 exception) statistical agreement among the charcoals and the analyzed mortars simultaneously, confirming the archaeological expectations for the Shayzar citadel. Results presented in this paper indicate good accuracy for the applied procedure for chronology reconstruction and highlight the capability of Cryo2SoniC to further characterize the Shayzar site.

### **INTRODUCTION**

Currently, radiocarbon chronology of archaeological sites is mostly based on the dating of organic materials uncovered during the excavations. The opportunity offered by mortars to establish the age of artifacts represents a sensitive improvement for the <sup>14</sup>C dating of archaeological buildings: mortar naturally records the act of building and represents also a class of materials virtually ubiquitous at archaeological sites, from the Neolithic period on (Rech 2004).

Mortar matrix can be schematically distinguished in 2 portions: the binder and the aggregates. The basis of the production of aerial mortar can be briefly summarized as follows: limestone (mainly CaCO<sub>3</sub>) is burned to quicklime (CaO) and is mixed with water to form slaked lime (Ca(OH)<sub>2</sub>). Slaked lime is then mixed with aggregates of different size and material type (e.g. reworked bricks, silica minerals, marble powder) and, during its hardening, lime mortar absorbs carbon dioxide (CO<sub>2</sub>) from the atmosphere to produce calcium carbonate (CaCO<sub>3</sub>). During mortar setting, contemporary air <sup>14</sup>CO<sub>2</sub> reacts with the slaked lime to form the calcite binder. Therefore, lime mortar binder represents a potential tool to assess the chronology of the different construction phases of buildings by means of <sup>14</sup>C dating.

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Since the 1960s, mortars have been exploited as a potential material for  $^{14}\text{C}$  dating (Delibrias and Labeyrie 1964), and despite the fact that this methodology appears very simple in its principles, some measured  $^{14}\text{C}$  ages showed evident contradictions with respect to the expected historic ages (Stuiver and Smith 1965; Baxter and Walton 1970; Van Strydonck et al. 1986, 1992; Ambers 1987; Heinemeier et al. 1997, 2010; Mathews 2001; Hale et al. 2003; Nawrocka et al. 2005, 2009; Lindroos et al. 2007).

Therefore, in order to eliminate observed biasing sources, sample preparation procedures have been implemented since the beginning of the mortar radiometric dating method (Delibrias and Libeyrie 1964). Most preparation procedures applied during recent decades consist of a combination of mechanical and chemical treatments (Folk and Valastro 1976; Cherf 1984; Van Strydonck et al. 1986, 1992; Heinemeier et al. 1997; Sonninen and Jungner 2001; Lindroos et al. 2007; Nawrocka et al. 2007, 2009; Goslar et al. 2009). The most common approaches involve the isolation of the binder atmospheric  $^{14}\text{C}$  signal by means of stepped acid digestion based on the evidence that binder carbonates react faster than limestone residuals. To our knowledge, the unique alternative to this methodology is based on the attempt to physically separate the binder carbonates by a combined mechanical/physical procedure (Folk and Valastro 1976; Heinemeier et al. 1997; Nawrocka et al. 2005; Ortega et al. 2012) based on the laboratory isolation of binder calcite.

The CIRCE (Centre for Isotopic Research on Cultural and Environmental Heritage) group developed a protocol based on a development of previously applied mechanical/physical procedures (Nawrocka et al. 2005) called CryoSoniC allowing  $^{14}\text{C}$  dating of mortars. This procedure, described by Marzaioli et al. (2011), was successfully applied to real lime lumps and, after implementation (Cryo2SoniC), to mortars leading to accurate results (Marzaioli et al. 2013). The main advantage of the Cryo2SoniC methodology is 1) the complete digestion of the laboratory isolated mortar fraction, avoiding difficulties in handling time-evolved fractions, and 2) the limited number of analyses per mortar to be performed: one for each sample after methodology accuracy evaluation. While usually in stepped acid digestions from 3 up to 5 aliquots of  $\text{CO}_2$  are produced by means of  $\text{H}_3\text{PO}_4$  (85 wt%) or  $\text{HCl}$  (standard solution 1.15 N), and analyzed for each sample (Van Strydonck et al. 1986, 1992; Heinemeier et al. 1997; Sonninen and Jungner 2001; Lindroos et al. 2007, 2012; Nawrocka et al. 2007, 2009).

The main aim of the Shayzar  $^{14}\text{C}$  dating project is to further improve the already built site chronology.  $^{14}\text{C}$  dating offers some unique advantages to the scientific community working on the site represented by the possibility to precisely define the site chronology using the properties of high-precision accelerator mass spectrometry (AMS) dating (Terrasi et al. 2008). AMS, in fact, in the range identified by a typical relative error on the isotopic ratios ( $\Delta R/R$ ) of 0.3%, allows  $^{14}\text{C}$  dating with a typical uncertainty of 25 yr, helping to clearly disentangle site development chronologies. Moreover, the possibility to directly date, by means of mortars, the manufacture of the structures represents a potential to avoid eventual biases due to the  $^{14}\text{C}$  analysis of organic materials found at the study site. For such materials, in fact, erroneous stratigraphic interpretation and/or on/offsite material reuse leading to age estimation biases cannot be estimated *a priori*, possibly adding extra costs to the development of the study (Bowman 1990; Van Strydonck 1986; Mathews 2001; Hale et al. 2003; Rech 2004).

In this study, the Cryo2SoniC procedure was applied to samples from the Shayzar citadel in Syria. Selected samples came from structures with well-constrained absolute chronologies, aiming to check our procedure potential to site age estimation. Moreover, the co-presence of intact charred wood fragments within the mortars was also used for this purpose as a further time reference.

Indeed, it is well established that while encased charcoals represent a matrix capable of leading to accurate mortar dating (Tubbs and Kinder 1990; Berger 1992; Van Strydonck 1992; Wyrwa et al. 2009; Heinemeier et al. 2010; Al-Bashaireh and Hodgins 2011), possible bias may be introduced due to their history.

To correlate eventual observed offsets with the technological characteristics of the analyzed samples, a series of analyses (i.e. TSOM, XRD, and SEM-EDS) were performed on mortars. They allow, through identification of mineralogical phases and nature of the aggregates, collecting clues about the presence of possible dating contamination sources. For example, the presence of recrystallized calcite plays a primary role in the accurate determination of  $^{14}\text{C}$  ages of the studied samples, raising the risk of rejuvenation in the case of weathering, or aging in the case of water table interactions. Other potentially dangerous identifiable features are calcination relics and biomicritic sand usage; their presence also leads to an aging effect on the final dating.

## ARCHAEOLOGICAL BACKGROUND

The archaeological site known as the citadel of Shayzar (35°16'N", 36°34'00"E) is located on the top of a hill overlooking the Orontes River in central Syria (Figure 1). The structure, partially buried, spans about 500 m N-S, 55 m E-W, and is located at ~220 m above sea level (asl). The citadel was founded in the 10th century on the ancient acropolis of a Hellenistic town originally called *Larissa on the Orontes* and later, in the Roman era, known as *Caesarea on the Orontes*. This fortification played an important military role in the region during the Medieval period, and only after the 15th century did Shayzar progressively lose its strategic function and gradually revert to a village. The remaining buildings represent a cohort of different construction phases that led to the fortification of the site between the 10th and 14th centuries, although the remains of previous structures were also incorporated into the walls of the citadel. The structures related to the Medieval fortification are better preserved on the edges of the plateau, with at least a ring of curtain walls, while the inner area was mainly occupied by the remains of the village belonging to the last phase of occupation (Tonghini et al. 2003, 2005, 2006, 2012).

Archaeological analyses of the remains revealed a clear stratigraphic sequence of the building phases, mostly anchored to a reliable relative chronology describing the temporal evolution of the fortification of Shayzar. This chronology was built by means of the features of masonry typology, stratigraphic data, and some absolute dating elements. Absolute time anchoring refers to 1) written evidence of historical sources and *in situ* inscriptions, 2) contextual data (e.g. pottery remains) retrieved from archaeological excavations, and 3) analogous structures already chronologically constrained from the same region. These data identify 7 periods in the development of the Shayzar site (Tonghini 2012):

- Period I: the earlier phase of occupation of the site covers probably from the 2nd century to the first half of the 10th century;
- Period II: the first fortification of the site from the second half of the 10th to the 11th centuries;
- Period III: from the end of the 11th century to the first half of the 12th century corresponding to the 1157 earthquake swarm;
- Period IV: the great restoration and strengthening of the defenses, from the start of the earthquakes to the early 13th century;
- Period V: a new defensive program, from 1233 to 1290;
- Period VI: partial modification and restoration of the fortification, from 14th to 18th centuries;
- Period VII: conversion of the site to residential use, from 19th century to 1950s.

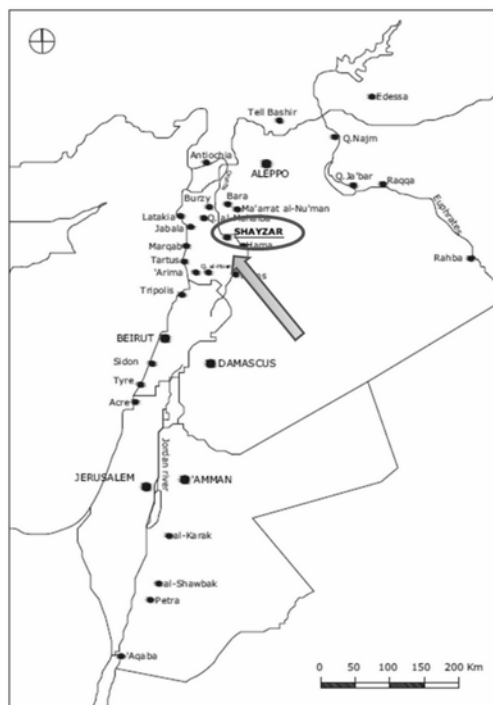


Figure 1 General map of Syria showing the location of Shayzar citadel.

## MATERIALS AND METHODS

### Sample Descriptions

All analyzed samples were collected from structures related to the fortifications (Figure 2) and identified by means of the code corresponding the archaeological code of building ambients (i.e. CF7, CF16, CF18, CF26). Ambient CF26 represents an ancient building, built before the construction of the citadel of the 10th century, later transformed in a defensive curtain in the eastern front between the end of the 10th and the 11th centuries. CF26 mortar was sampled from the remains of wall US 5035 of the same building belonging to its oldest part and, hence, attributable to Period I. Sample CF7 (Figure 2) comes from the top of the vault of wall 6254, inside space 16 of building CF7, in the area of access to the citadel. Building CF7 corresponds to a massive defensive structure on several levels known in the literature as *glacis*; at Shayzar it is attributed to the second half of the 12th century (Period IV). Samples CF16 (from the nucleus of wall US 3008) and CF18 (from the nucleus of wall US 3217) have been collected from 2 towers of the eastern defensive curtain, both attributed to the second half of the 12th century (Figure 2). Their construction postdates the strong earthquake swarm to the end of Period III.

### Mortar Characterization

Samples CF7, CF16, and CF18 underwent characterization. CF26 was not analyzed because of its complete consumption during  $^{14}\text{C}$  dating, but according to its macroscopic aspect, it is presumed to be similar to the others. Information on the composition of both the binder and the aggregates has been obtained by TSOM, XRD, and SEM-EDS analyses of these samples. Mineralogical-petro-

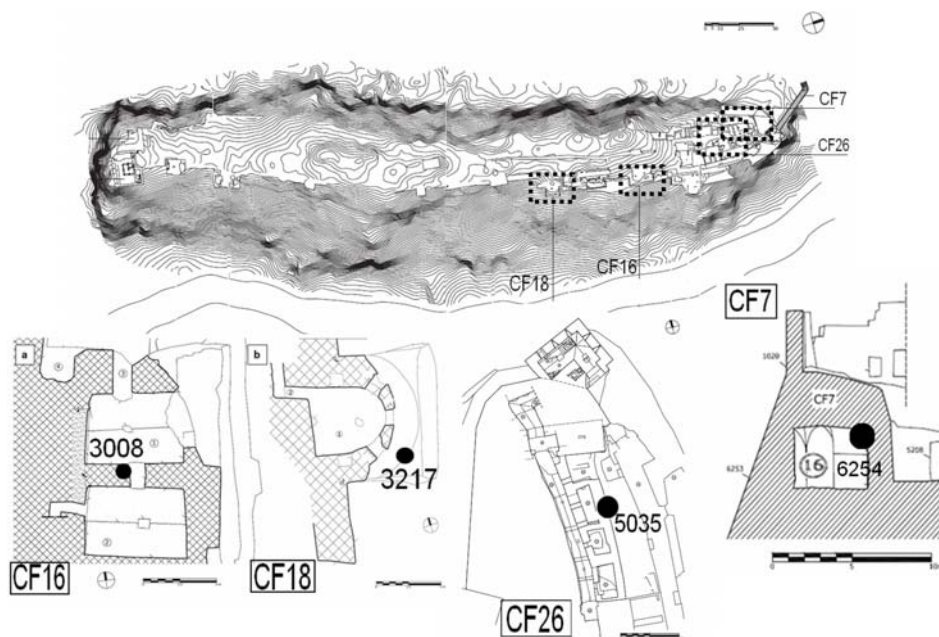


Figure 2 Plan of the Shayzar citadel showing the sampling zones

graphic analyses were aimed to identify 1) the nature of the binder, 2) the occurrence of unburned limestone residues and calcareous aggregates, and 3) the occurrence of recrystallized calcite.

TSOM was performed on thin sections (30  $\mu\text{m}$  thick) with an optical polarizing microscope under parallel and crossed nicols. A Camscan MX 2500 SEM microscope equipped with a LaB6 electron source and an energy dispersive X-ray detector (EDS) was used to collect elemental and structural microanalyses, which gave valuable information on the mineral phase composition and the pore structure of the historic mortars (Figure 3). Previously used thin sections were covered with an ultrathin coating of graphite to prevent the accumulation of static electric fields during imaging. Qualitative spectra interpretations were performed through SEMQuant Phizaf software.

XRD analyses were performed with a Philips X'Pert diffractometer in Bragg-Brentano geometry equipped with a Cu X-ray tube operating at 40 kV and 40 mA ( $\text{CuK}\alpha$  radiation), and an X'Celerator detector, both mounted on a PW1050/37 theta-2theta vertical goniometer. Data acquisition was performed by operating a continuous scan in the range  $3.01\text{--}79.99^\circ$  [20], at an acquisition rate of  $0.02^\circ$  per second [20]. Diffraction patterns were interpreted with X'Pert HighScore Plus 3.0 software by PANalytical, reconstructing mineral profiles of the compounds by comparison with ICDD and ICSD diffraction databases. XRD analyses were focused on the fractions of the samples with grain size below 63  $\mu\text{m}$ . These fractions were collected, broken up by means of soft hammering, and then dry sieving mortars samples, across a series of dry test sieving (800, 160, and 63  $\mu\text{m}$ ), until the accumulation of 0.25 g of powder, virtually representing the binder fraction. The obtained sample was crushed in an agate mortar before XRD analyses.

#### **$^{14}\text{C}$ Analyses**

Cryo2SoniC methodology was applied to suppress the C contamination in the analyzed mortar samples by means of a sequence of physical separations: cryobreaking, ultrasonication, and centrifuga-

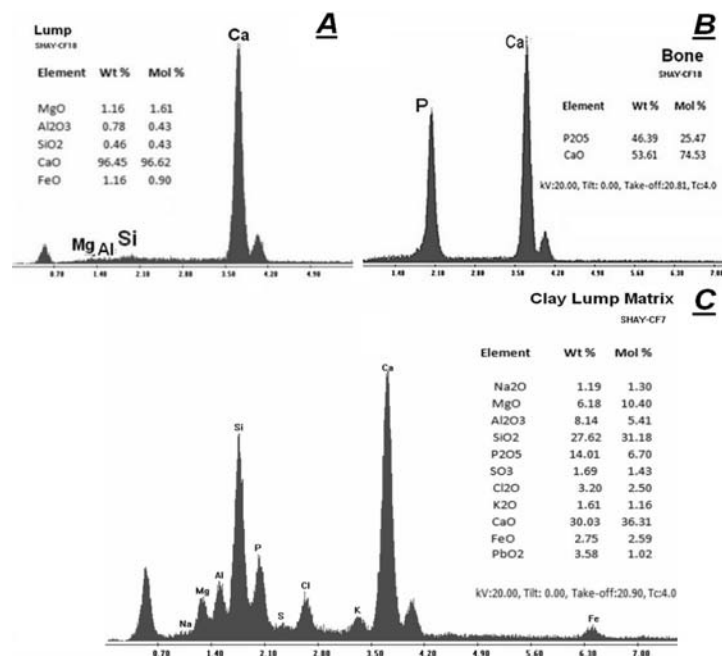


Figure 3 EDS spectra of the core of a lump (A) and of a bone fragment (B) inside sample CF18, and of a clay lump inside sample CF7 (C).

tion (Marzaioli et al. 2013). This procedure is based on the experimental observation that binder carbonates are characterized by an easily breakable structure under a series of ultrasonic attacks. This main selection criterion results from the ultrasonication allowing the isolation of the binder signal from the unburnt limestone residuals by breaking the softer binder structure and originating a suspension of fine particles characterized by a slow sedimentation velocity and, hence, easily recoverable by means of centrifuging. Marzaioli et al. (2011) successfully tested a protocol (CryoSoniC) based on a single step of ultrasonication of 30 min on synthetic mortars, not containing aggregates, and lime lumps. Archaeological mortars are usually produced by adding some aliquots of eventually fine-grained, calcareous aggregates. An improvement to the methodology (Cryo2SoniC) was necessary in order to analyze real samples. This procedure revealed good accuracy also for real mortars (Marzaioli et al. 2013). In this study, Cryo2SoniC involves a double step of ultrasonication, producing different time-evolved suspension fractions from the same mortar matrix. The procedure parameters (i.e. timing) were tuned on experimental age vs. time of suspension evolution profiles. These profiles evidenced, for some mortars, a sudden aging of initially produced suspensions (for 10 min) and an overall rejuvenation of successively produced suspensions, with no statistical difference on suspension ages produced after 30 min and up to 50 min. Data were interpreted as fine carbonaceous aggregates suddenly entering the suspension. These materials, significantly aging the initial suspensions were accurately removed from the samples after 10 min of ultrasonication, producing the so-called Cryo2SoniC *susp\_sand* fraction. In detail, the applied procedure was

1. **Cryogenical breaking.** Following the procedure reported by Nawrocka et al. (2005) and Marzaioli et al. (2011), mortar pieces (~5 g) were submerged in liquid nitrogen until the achievement of thermal equilibrium and immediately transferred into an oven at 80 °C for several minutes. After repeating this freezing/thawing cycle 3 times, the mortars were broken by gentle hammering.

2. **Size selection.** The produced fragments (spanning a wide range of particle size) were sieved and only particles with size below 800  $\mu\text{m}$  were selected and stored in a 75-mL beaker. Then ~40 mL of deionized/decarbonated water (DDW) was added.
3. **1st ultrasonic selection.** After complete sedimentation (~12 hr), the selected powder was re-wetted with 40 mL of DDW and ultrasonicated for 10 min. DDW-containing suspended mortar particles were totally removed and transferred to a Falcon 50-mL centrifuge tube. This fraction of binder represents the fraction potentially affected by dead carbon contamination (*susp\_sand*) due to the probable presence of very fine carbonaceous grains sands entering the suspension easily and before binder particles.
4. **2nd ultrasonic selection.** Residual powder, decanted on the bottom of the beaker after the first sonic attack and the total removal of *susp\_sand*, underwent another ultrasonication for 30 min in an excess (~40 mL) of DDW. About 30 mL of water was collected by siphoning and stored in another Falcon centrifuge tube, taking great care not to induce a new suspension of the sediments. This last fraction, according to our experimental experience, represents the suspension guaranteeing accurate dating (*susp*).
5. **Centrifugation.** The Falcon centrifuge tube containing *susp* carbonates, and the other containing the *susp\_sand* fraction, were centrifuged at 8.0 krpm in a rotor of 10 cm mean radius for 5 min and oven-dried overnight (80 °C).

About 40 mg of *susp* and *susp\_sand* fractions and carbonate standards samples (i.e. IAEA C1 and C2; Rozanski et al. 1992) were digested under vacuum to  $\text{CO}_2$  by means of a complete orthophosphoric acid attack (McCrea 1950) for 2 hr at 85 °C. Charcoal samples found in mortars were mechanically extracted and pretreated according to a modification of Berger's (1992) protocol. Since our samples were easily recognizable and extractable, we applied the conventional AAA (acid-alkali-acid) method (Passariello et al. 2007) with a longer (following Berger's observations) time (12 hr) for the first acid digestion in order to completely remove calcite contaminations, eventually evolving to  $\text{CO}_2$  during the successive combustion phase. Treated charcoals underwent combustion in a run together with normalization/check standards (i.e. IAEA C3 and C5 (Rozanski et al. 1992) and NIST OxII) and background (graphite) samples according to Marzaioli et al. (2008). The developed  $\text{CO}_2$  (both from combustion and acid digestion) was cryogenically purified by other gases, reduced to graphite on iron powder catalyst according to the CIRCE sealed-tube reaction protocol (the zinc process) following Marzaioli et al. (2008), and analyzed to measure  $^{14}\text{C}$  isotopic ratios using the CIRCE AMS system (Terrasi et al. 2008). Measured  $^{14}\text{C}$  ratios were converted to  $^{14}\text{C}$  ages (Stuiver and Polach 1977) and calibrated to absolute (i.e. calendar) ages by means of the CALIB v 6.0 program (Stuiver and Reimer 1993) using the IntCal09 atmospheric calibration data set (Reimer et al. 2009). All  $^{14}\text{C}$  dates in this paper are reported as intervals comprised between the highest/lowest calendar age identified by the projection of measurement intervals (1 or  $2\sigma$ ) on the absolute age axes using the IntCal09 calibration curve.

## Data Analysis

In this study,  $^{14}\text{C}$  ages with dispersion coefficients ( $2\sigma$ ) are compared with charcoal  $^{14}\text{C}$  ages at  $2\sigma$ .  $^{14}\text{C}$  calibrated ages at  $2\sigma$  for both mortar and charcoals were compared with archaeological expectations. A  $t$  test for the means was used to compare these results. The  $t$  test indicates no difference between the means if the level of agreement observed lies within 0.05 and 0.95 which, from here on, will be conventionally called the  $2\sigma$  level. When explicitly stated, given a number of  $^{14}\text{C}$  dates referring to coherent samples, the weighted mean of these ages calibrated using IntCal09 is referred to as calibrated weighted age. The calibrated weighted age dispersion is used to estimate the error of the weighted average if a  $\chi^2$  test on the significance of the weighted mean at 0.05 was successful.



## RESULTS AND DISCUSSION

### Mortar Characterization

All analytical techniques performed were necessary to infer the nature of mortars and their characteristics and if they possibly interfere with  $^{14}\text{C}$  dating, such as the co-presence of other calcite sources (i.e. carbonatic aggregates, calcination relicts, or secondary depositions) together with the binder. Macroscopically, all mortar samples show an arenaceous appearance, strong cohesion, and a great abundance of charcoals. Microscopic examinations of the samples show a micritic aspect of the binder carbonate, a homogeneous texture, and a limited amount of sandy aggregates. Therefore, all samples can be classified as fat mortar because of their high binder/aggregate ratios. The results of XRD analyses show that the calcitic binder contains small amounts of magnesium carbonate due to the presence of dolomitic rock fragments (Table 1). Uniformly distributed aggregate is scarce and mainly composed of these dolomitic rock fragments, quartz, biotite grains, a local sand essentially composed of organogenous scraps (*Globigerina* and mollusks), and some biomicritic-globigerina-limestone microfragments. Small fragments of pottery and some minerals of volcanic origin, such as diopsides and zeolites, are dispersed in the binder matrix, together with some clay lumps. These clay lumps contain dispersed chloride salts (halite and sylvine), charcoals, and microfragments of bones (60–300  $\mu\text{m}$ ). In particular, their presence has been confirmed by SEM-EDS results highlighting the presence of apatite. The simultaneous occurrence of clay, charcoal, and phosphate minerals in clay-lumps systems suggests their origin from a different site than the sands, which come from the Orontes River basin according to a previous study (Tonghini 2012). Sporadic crystals of gypsum have been found only in sample CF7. The presence of secondary calcite microcrystals and chlorine salt crystals, in all mortar samples, has been observed in the voids. These features were attributed to restoration and conservation works by Tonghini (2012), but they are more probably ascribable to weathering. Abundant lime lumps of different sizes, showing shrinkage cracks, have been recognized in all samples; however, only some of them contained calcination relicts.

Table 1 Mineralogical composition by XRD (+++ major phase, ++ secondary phase, + minor phase, (+) traces).

	CF7	CF16	CF18
Calcite	+++	+++	+++
Dolomite	++	+	++
Sylvine	(+)	(+)	(+)
Halite	(+)	(+)	(+)
Quartz	(+)	(+)	(+)
Apatite	(+)	(+)	(+)
Diopside	+	+	+
Gypsum	(+)	–	–

### $^{14}\text{C}$ Dating

Mortars have been dated with the aim of confirming and improving the precision of ages of the construction phases of the Shayzar military citadel. Results are summarized in Table 2 and Figure 4, where  $^{14}\text{C}$  ages of both fractions (i.e. *susp* in bold and *susp\_sand*) obtained from Cryo2SoniC procedure are shown for each mortar sample, together with charcoal dates and archaeological expectations. According to the *susp* results shown (Table 2), an overall different age phasing is recognizable: CF7, CF16, and CF18, which identify a later development of the castle (Period III), and CF26, which marks the beginning of the Shayzar fortification (Period I). The calibrated ages of samples CF7, CF16, and CF18 do not differ among each other at a  $2\sigma$  level. They identify a building phase

with a calibrated weighted age of AD 1022–1278 ( $2\sigma$ ) in agreement with archaeological expectations for the sampled structures and the earthquake swarms discontinuity of AD 1157 representing the end of Period III. The same level of agreement ( $2\sigma$ ) was observed for each individual sample with respect to expectations.

Table 2  $^{14}\text{C}$  dates of mortars and charcoals. For each analyzed mortar, both *susp\_sand* and *susp* results are shown. Calendar ages ( $1\sigma$  and  $2\sigma$ ) are represented as a continuous distribution spanning the maximum and minimum calibrated values.

Sample	Analyzed fraction	$^{14}\text{C}$ age (BP)	Calibrated age AD		Archaeological age AD
			$1\sigma$	$2\sigma$	
CF7	Susp_sand	$1407 \pm 41$	610–658	568–674	12th century
	Susp	$1017 \pm 65$	902–1151	887–1169	
	Charcoal	$869 \pm 22$	1163–1209	1051–1221	
CF 16	Susp_sand	$737 \pm 45$	1228–1290	1211–1386	12th century
	Susp	$868 \pm 26$	1160–1213	1047–1251	
	Charcoal	$923 \pm 45$	1041–1158	1025–1208	
CF18	Susp_sand	$405 \pm 35$	1441–1614	1432–1630	12th century
	Susp	$729 \pm 54$	1225–1296	1187–1392	
	Charcoal	$882 \pm 26$	1058–1211	1045–1219	
CF26	Susp_sand	$1400 \pm 27$	623–658	603–665	10th century
	Susp	$1150 \pm 35$	784–968	779–976	
	Charcoal	$1376 \pm 53$	608–683	569–771	

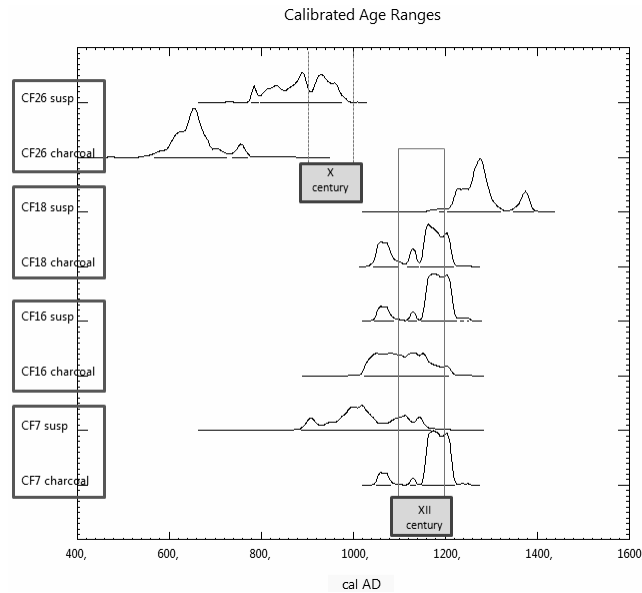


Figure 4 Calibrated dates of each sample (susp and charcoal) with the corresponding archaeological reference.

The same analysis procedure for the *susp\_sand* fractions led to a calibrated weighted age of AD 600–1798 ( $2\sigma$ ), again in agreement with the archaeological estimation, but characterized by a drastic failure of the  $\chi^2$  test for the significance of the weighted mean due to a sensitive scatter of the *sand-susp*  $^{14}\text{C}$  ages. For the *susp\_sand* class samples, it should be noted how 2 of these fractions

were  $^{14}\text{C}$  enriched (younger) with respect to the relative *susps* (CF16 *susp\_sand* and CF18 *susp\_sand*) and one was depleted (CF7). A similar behavior is shown by the CF26 calibrated dates. The CF26 *susp* calendar age was in agreement with the castle archaeological chronology, while CF26 *susp\_sand* gave sensitive age overestimation.

Since IAEA C1 and C2 reference materials are routinely used as quality control for Cryo2SoniC quality assurance purposes (they undergo the same pretreatment of mortars), giving no statistical difference from the same materials conventionally treated, any possibility of dissolved inorganic carbon contamination (i.e. rejuvenation) due to the wet attack of ultrasonication can be ruled out *a priori*. Hence, observed  $^{14}\text{C}$  fluctuation for all the *susp\_sand* fractions can be interpreted as a different relative influence of biomicritic microfragments (aging effect) and calcite recrystallization crystals (rejuvenation effect). However, more detailed analyses on the *susp\_sand* fraction should be performed in order to determine such behavior. These results highlight how the *susp\_sand* fraction is generally much more sensitive, with respect to *susp*, to any interfering contaminant introducing also a particular sensitivity to secondary calcite. These observations strengthen our assumption that the *susp* fraction is the most reliable Cryo2SoniC fraction guaranteeing accurate dating.

Looking at the charcoal results, a similar picture is observed: 2 different phases can be identified, charcoals from CF7, CF16, and CF18 belong to a phase coherent with the castle Period III (i.e. calibrated weighted age of AD 1051–1216), while charcoal CF26 alone is dated to AD 569–771. For this kind of material, while matching with expectations is clear for the samples referring to Period III, a statistically significant (i.e. more than  $3\sigma$ ) aging of the sample CF26 is observable. This result is probably attributable, excluding calcite contamination because of the prolonged HCl attack applied during its pretreatment phase, to the CF26 charcoal history. Bowman (1990) also points out this phenomenon as a non-neglectable occurrence when analyzing charcoals encased in mortars.

Regarding the comparison between observed results ( $^{14}\text{C}$  ages) from charcoals and *susp* fractions, a lighter agreement (always comprised between  $2\sigma$  and  $3\sigma$ , becoming  $<2\sigma$  after calibration) is observed with the exception of CF26 being significantly older than the relative analyzed *susp*. Again, this observed mismatch is likely due to wood pre-aging before its usage for mortar production. The observed results are evidence of how  $^{14}\text{C}$  dating of mortar via Cryo2SoniC represents an accurate and precise tool for further deepening the characterization of the Shayzar study site.

## CONCLUSIONS

Despite the simplicity of the carbonation process leading to the absorption of contemporary  $\text{CO}_2$ , mortar matrices represent a complex system frequently containing other carbonaceous sources mixed in different aliquots, making the  $^{14}\text{C}$  dating of archaeological mortars a difficult task. Efficient extraction methods to isolate the binder (the mortar carbonate fraction merely attributable to carbonation) are necessary in order to prevent the determination of biased ages. In this framework, the Cryo2SoniC procedure and its further developments were tested to obtain reliable binder fraction isolation. The Cryo2SoniC protocol was applied to mortars sampled from the ancient ruins of the Shayzar site and a series of petrographic characterizations were also performed in order to elucidate mortar production technology. These analyses confirmed the co-presence of both micritic sands and reprecipitated calcite.

The observed results on *susp\_sand* fractions indicate their strong sensitivity to possible biasing agents, confirming the overall more stable and accurate character of the *susp* fractions. In fact, all the calendar ages for this fraction were in statistical agreement with the archaeologically developed absolute chronology for this site.

The co-presence of mortar-encased charcoals also allowed independent estimation of the analyzed sample chronology. The observed results pointed out a general agreement of charcoals vs. *susp* fractions, with the exception of the CF26 sample where only Cryo2SoniC mortar analysis allowed accurate  $^{14}\text{C}$  dating. The application of the Cryo2SoniC protocol showed promising results for accurate determination of the Shayzar chronology, indicating that this method is a promising tool for further mortar  $^{14}\text{C}$  dating.

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