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Estimation of the Age of Architectural Heritage Objects by Microstructural Changes of Calcite in Lime Mortars of Ancient Brickwork and Masonry

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Citation: Kotlyar, V.; Pishchulina, V.; Beskopylny, A.N.; Meskhi, B.; Popov, Y.; Efremenko, I. Estimation of the Age of Architectural Heritage Objects by Microstructural Changes of Calcite in Lime Mortars of Ancient Brickwork and Masonry. *Buildings* **2021**, *11*, 240. https://doi.org/10.3390/buildings11060240

Academic Editor: Jorge de Brito

Received: 24 April 2021
Accepted: 2 June 2021
Published: 4 June 2021

Abstract: Determining the age of ancient architectural and cultural monuments is a significant scientific problem. An approach based on the transformation of portlandite into calcite and subsequent recrystallization of calcite is considered, which allows for estimating the relative age of ancient brickworks for local groups of historic buildings based on the results of diffraction studies of powder samples of carbonate mortars and measurements of samples with a known age. This article presents the results of the study of lime mortars of ancient brickwork. Under natural conditions, the process of transformation of portlandite into calcite takes from 100 to 200 years. The rate of this process is influenced by temperature, humidity, peculiarities of interaction with carbon dioxide contained in the air, etc. Examples show that portlandite is completely transformed into calcite in masonry mortars of the 18th century and that portlandite is not found in older mortars. It was determined that after the transformation of portlandite into calcite, an increase in the degree of recrystallization of calcite is observed, which manifests itself in powder diffraction patterns in the relative broadening of the diffraction peak of calcite hkl 104. In a detailed study, an estimate of the peak width at half maximum (FWHM) associated with the degree of crystallinity is effective. The actual data are given, which show that in older lime mortars the degree of recrystallization of calcite is higher than in younger ones. This fact makes it possible to indirectly determine the relative age of brickwork and masonry of various buildings of architectural heritage, which is especially relevant for the objects with the use of lime mortars of the northern provinces of the Byzantine Oecumene and other periods of various cultures.

Keywords: medieval architecture; dating method; medieval mortar; portlandite; calcite; recrystallization of calcite; X-ray powder diffraction

1. Introduction

Lime binders (air and hydraulic lime, Roman cement) and masonry mortars based on them are among the first to be widely used by humanity in its construction history to construct brick and masonry. Lime mortars became a mass and ubiquitous building material during the period of the Roman Empire. Lime-based mortars and lightweight concrete (LC) have been used successfully since ancient Roman times and have gained popularity due to their excellent physical and technical properties [1].

In past centuries, the widespread use of lime mortars is primarily due to their properties, relatively simple production technology, and relatively widespread distribution of raw materials for their production—various carbonate rocks (limestones) and small aggregates.

Most people who look at ancient brick or masonry in architectural heritage sites always ask questions: "When was it done? When was it built?" However, it is not so easy to answer this question correctly. Estimating the age of ancient historical, cultural, and architectural heritage is a complex and essential scientific problem and requires an integrated approach and the use of various research methods.

Non-destructive methods [2,3] were applied to investigate historic stone and brickwork characteristics without compromising the artistic value of the monumental building. In [2] sound tests were used to characterize the stone walls at the Sanctuary of Santa Maria Delle Grazie in Varoni, which revealed the texture and structure of the masonry. The authors also confirmed the ineffectiveness of strengthening it with mortar injections.

The problem of estimating the age of lime mortars affects not only historical and cultural aspects but also archaeological ones since organogenic limestones with various calcite fossils were often used to obtain them. In [4], evidence of the widespread use of organogenic limestones was presented to produce lime mortars and indirect signs of determining their age. In [5], radiocarbon dating methods were used for historical stone structures containing organic remains. The sampling methods for radiocarbon dating of mortars were presented.

Determining the age of structures is especially important for specialists in architecture, archaeologists, and historians. Knowing the absolute or even relative age of ancient building objects, experts can draw many reliable conclusions in their fields of knowledge. In [6,7], comprehensive studies were carried out to study medieval lime mortars using chemical, petrographic and X-ray phase analyzes. Lime mortars of ancient buildings in Russia, Armenia, Georgia, Greece, Turkey, Abkhazia, and other regions have been investigated. The results of studies, for example, confirmed the estimated dates of the foundation of the second line of defense of the Anakopia fortress within 570–580 years, the reconstruction of the gate tower in 910–930, and the entrance gate around the year 950. Analysis of the lime mortars of the church near Anakopia (Akuah temple) gave the time of construction from 650–680. The method proposed by the authors for determining and clarifying the age of brick and masonry based on lime mortars made it possible to revise the existing approaches to the dating of some cultural heritage sites. Currently, in the history of architecture and archaeology, there are many direct and indirect methods for determining the age of particular ancient building objects:

- Historical and architectural methods: [8,9] calendar, typological, stratigraphic dating, serialization, etc.;
- Physical and chemical methods [10,11]: thermoluminescence method, electron paramagnetic resonance method, dating by remanent magnetization, by the racemization of amino acids, radiometric, potassium-argon dating, etc.

The possibility of using the thermoluminescent method for dating fossilized paleontological remains of animals was investigated in [12]. The authors note a relatively simple application and a wide range of chronological periods during which the process gives reliable results with minimal errors. Using the thermoluminescent method, the authors determined the different ages of the studied mammoth remains from 12,000 to 100,000 years. However, it is known that the thermoluminescent method works well over long time intervals [13] and leads to significant errors in small ones—for an age of up to 1000 years, the method leads to significant errors.

The radiocarbon dating method for organic remains by measuring the content of the radioactive isotope ^{14}C in the material concerning the stable isotopes of carbon is now widespread. The changes in atmospheric CO_2 as a result of anthropogenic activities were investigated in [14]. Samples of leaves of evergreen and deciduous trees as well as seasonal leaves of small plants in CO_2-emitting industrial sites were analyzed. The data showed that the concentration of ^{14}C in the study areas was significantly lower due to the emission of anthropogenic CO_2 than in the clean area.

Problems of radiation effects on binders and the subsequent study of the radiation background were investigated in [15]. X-ray diffraction, polarized light microscopy, and other techniques were applied in [16] to investigate the raw materials used in the paintings in the Taitung Tomb. The authors showed that some of the architectural murals were re-painted in the mid to late 19th century. The mortar layer consisted of brick ash (albite, gismondine), portlandite, tung oil, and flour.

Age-related petrographic analysis of mortar samples from Roman monuments, including Portico Emilia, Temple of Concordia, Temple of Dioscuri, Temple B, and other structures, were carried out in [17]. The authors examined the volcanic rocks used in the mortars of the buildings of ancient Rome from the beginning of the second century BC to the early imperial era to establish their pyroclastic origin (Pozzolane Rosse). The critical issues in the study of mortars are usually their strength characteristics [18–20], which are also determined by non-destructive methods [21,22].

The effect of moisture on the specific gravity of masonry walls made of ceramic bricks and lime mortars of various monuments of architectural heritage was studied in [23]. Experimental studies of ageing clutches have been carried out. It has been shown that moisture penetration causes an increase in masonry weight by more than 20%. This indicator can be used in the general structural assessment of historic stone buildings. Determination of the characteristics and durability of mortars for their correct use and preservation of architectural monuments and historical heritage was carried out in [24]. The authors studied mortars based on lime–metakaolin and hydraulic lime–metakaolin with the addition of nano-TiO_2 and perlite. It is shown that mortars with pearlite and nano-TiO_2 are the most effective, making them suitable for preserving cultural heritage sites.

Samples of mortars from Arslantepe (Turkey) provide unique information on the production and use of lime during the late Eneolithic period (4th millennium BC). A versatile approach to the study of lime mortars was carried out in [25], including polarized light microscopy, X-ray powder diffraction, and scanning electron microscopy combined with energy dispersive spectroscopy, was used to characterize objects from the Late Chalcolithic 3–4 (3800–3400 BC). Similar research methods based on X-ray fluorescence analysis, X-ray diffraction analysis, and scanning electron microscopy of building mortars were carried out in [26]. Their compatibility and effectiveness have been shown for masonry and plastering materials to restore historically valuable buildings.

The hardening process of lime concrete and mortars takes place in several stages, according to the generally accepted theory. The first stage, which lasts about a month, is characterized by the formation of calcium hydroxide crystallites (portlandite) according to the reaction:

$$CaO + H_2O = Ca(OH)_2 \quad (1)$$

with further accretion of the formed crystals. The second stage is characterized by the strengthening of crystalline intergrowths of calcium hydroxide due to its reaction with carbon dioxide present in the atmosphere:

$$Ca(OH)_2 + CO_2 + H_2O = CaCO_3 + 2H_2O \quad (2)$$

In the process of carbonation, chemically bound water is released. Therefore, in the first 1–2 years, lime mortars seem to be moist all the time. In the course of this reaction, in the beginning, a dense outer layer of calcium carbonate (calcite mineral) forms, which makes it difficult for carbon dioxide to penetrate deep into the masonry, and the process slows down significantly but still continues, since lime mortars have sufficiently high porosity. Gradually, all of the portlandite turns into calcite with an increase in the stability and strength of the mortar. The carbonation process is well known and studied during the natural carbonation of concretes on Portland cement and the production of silicate concretes with forced carbonation [27–29]. These processes, the formation of portlandite, and subsequent carbonation to precipitate polymorphs of calcium carbonate are well covered in the literature [30].

The carbonation of portlandite ($Ca(OH)_2$) depends on many technological factors: the dispersion of lime particles, the water content of the mortar, temperature fluctuations, the concentration of carbon dioxide, as well as the presence of substances that contribute to an increase in the concentration of CO_2 inside the crystallizing mass. For example, by introducing organic materials: milk, blood, the decoction of tree bark, etc., as practiced by ancient Russian masters, as well as the time of carbonation. The last of the listed factors is decisive at the recrystallization stage when the environmental parameters are relatively uniform. Changes in atmospheric CO_2 content and seasonal temperature fluctuations can be neglected on the scale of estimates at the level of decades centuries. Only additional long-term humidification is essential, which promotes the dissociation of carbonates and bicarbonates with carbonic acid and the activation of ion-exchange reactions in the liquid phase.

In parallel with carbonation, the mortar can gain strength due to the interaction of calcium hydroxide with reactive varieties of silica, which is present in various rocks and ceramics-volcanic tuff and volcanic ash, siliceous opal-cristobalite rocks, volcanic acid rocks, ceramic battle and others [31,32]. These rocks and materials can act as fine aggregates and as a component of a binder, as a result of which hydrosilicates of calcium are formed with a variable water content according to the reaction:

$$Ca(OH)_2 + SiO_2 = CaO \times SiO_2 \times nH_2O \tag{3}$$

The last and longest stage of the "life" of a lime mortar is the stage, conventionally called the stage of recrystallization of calcite, accompanied by the growth of calcite microcrystals and an increase in the degree of structural ordering of the crystal lattice.

In [33] Optically Stimulated Luminescence (OSL) was applied to determine ages of mortar samples from the internal layers of the complex Holy Aedicule structure of the Holy Sepulchre in Jerusalem. OSL was accompanied by X-ray Fluorescence (XRF), Scanning Electron Microscopy with Energy Dispersion X-ray Analysis (SEM-EDS), and X-ray diffraction (XRD).

It is known that after the manufacture of ceramic products, including ceramic bricks, nothing happens to them in physicochemical, phase, and mineralogical transformations that could help determine the age. The age of brickwork and, accordingly, of one or another ancient building is determined by the type and marking (stigma) of products, the kind of masonry mortar, features of brickwork, taking into account the geographical specifics and regional signs of brick construction, confirmed by historical data, etc. However, with regard to the use of ceramic bricks in the past, the reuse of bricks was widespread in construction. Moreover, if practically nothing happens to fired ceramic bricks for centuries, then the lime mortar is subjected to significant chemical and mineralogical transformations, by which the age of the brickwork can be indirectly determined.

Thus, the purpose of this work is to develop a method for the relative determination of the age of brick and masonry by the degree of recrystallization of calcite in lime mortars, which, in combination with existing methods, will make it possible to determine and clarify the age of the masonry and, accordingly, the age of cultural heritage objects.

2. Materials and Methods

For research, samples of lime mortars at various objects of the architectural heritage of the South of Russia and abroad—Abkhazia, Turkey, Armenia, Georgia, and Greece (Figures 1–4)—were selected. A total of 158 samples were selected and examined. Several pieces were taken from each object. Objects for research were classified into "standard of comparison", for which there are convincing architectural studies, and they are dated by researchers, archaeologists, and architects, and "controversial", for which there is no accurate and generally accepted dating data.

When taking samples, conditions for the location of mortar samples in the masonry and the following factors were taken into account:

– Wet or dry conditions;
– Sunny side or darkened conditions;
– Underground or aboveground part of the structure;
– Access to carbon dioxide and moisture from the air;
– Temperature conditions.

These factors were taken into account because, as is known, the rates of chemical reactions, and accordingly, the transformation of portlandite into calcite and its recrystallization, largely depend on temperature and humidity. The samples of natural carbonate rocks were also studied near the sampling sites and from which lime was most likely obtained for mortars.

(a)

(b)

Figure 1. Fragments of brickwork on lime mortar in Chersonesos (Crimea): (**a**) The undestroyed part of the brickwork; (**b**) Destroyed part of brickwork.

(**a**)

(**b**)

Figure 2. Dilapidated brickwork on lime mortar in the ancient city of Ephesus (Turkey, II century AD): (**a**) Partly preserved brick and stone facade of the building; (**b**) Fragment of the destroyed brick arch.

(**a**)

(**b**)

Figure 3. Fragments of brickwork on lime mortar at the objects of the architectural heritage of Abkhazia; (**a**) Anakopia, gate tower, 10th century; (**b**) Bzyb fortress, wall, 8th century.

(**a**)

(**b**)

Figure 4. A dilapidated brick vault on lime mortar in the ancient city of Sardis (Turkey IV-V centuries): (**a**) Fragment of the fortress wall; (**b**) Brick arch.

The degree of development of recrystallization of calcite can be revealed by instrumental X-ray diffraction and electron probe methods, which effectively study microcrystalline aggregates. Analysis of diffraction patterns allows us to control the degree of recrystallization of micro calcite formed due to portlandite.

During sample preparation and separation of secondary calcite, the minimum content of other minerals and rocks (quartz, sandstones, etc.) was achieved. If carbonate rocks (which is quite rare) were used as a mortar filler, then the technique was used to exclude the ingress of primary (limestone) calcite into the sample or to achieve its minimum content (less than 2–3%). In the studied samples of ancient mortars in 95% of cases, quartz sand and, to a lesser extent, various igneous and metamorphic non-carbonate rocks were used as fillers. Samples for X-ray studies were single-phase, consisting of calcite formed from portlandite. In any case, limestone has a significantly greater strength in comparison with a binder mass and fractional composition of more than 0.1 mm. Therefore, it is easily released during sample preparation. It is also clearly visible when studying thin sections under an optical polarizing microscope. Its absence in samples for X-ray analysis was strictly controlled.

Instrumental studies were carried out using the methods that provide information on samples of carbonate mortars' composition and microstructural features. Electron probe studies were carried out on a Tescan LMU scanning microscope (TESCAN ORSAY HOLDING, Brno, Czech Republic) with an INCA Energy 450/XT (Oxford Instruments plc, Abingdon, UK) energy dispersive microanalysis (EDX) system. Aggregates of masonry deposited with carbon were studied. Diffraction studies were performed on an ARLX'TRA diffractometer (Thermo Fisher Scientific, Ecublens, Switzerland) with a horizontal flat sample. The characteristic radiation of the copper anode was used (wavelength CuKα1 1.5406 Å), scanning speed 5 deg/min, voltage 35 kV, current 30 mA.

Electron probe study of the microstructure of masonry material samples reveals the presence of morphologically different calcite aggregates in their composition: (1) relatively large particles (more than 50–100 microns in size), as a rule, characterized by an admixture of magnesium characteristic of natural carbonates, which are fragments of carbonate building materials; (2) the main microporous carbonate mass formed by microcrystals and aggregates (less than 0.5 μm) of calcite, among which there are rare well-faceted crystals of authigenic magnesium-free (with an analytical sensitivity of about 0.05 wt%) micron-sized calcite (sometimes reaching a size of about 10 μm) and insignificant the amount of clay and quartz material (Figure 5).

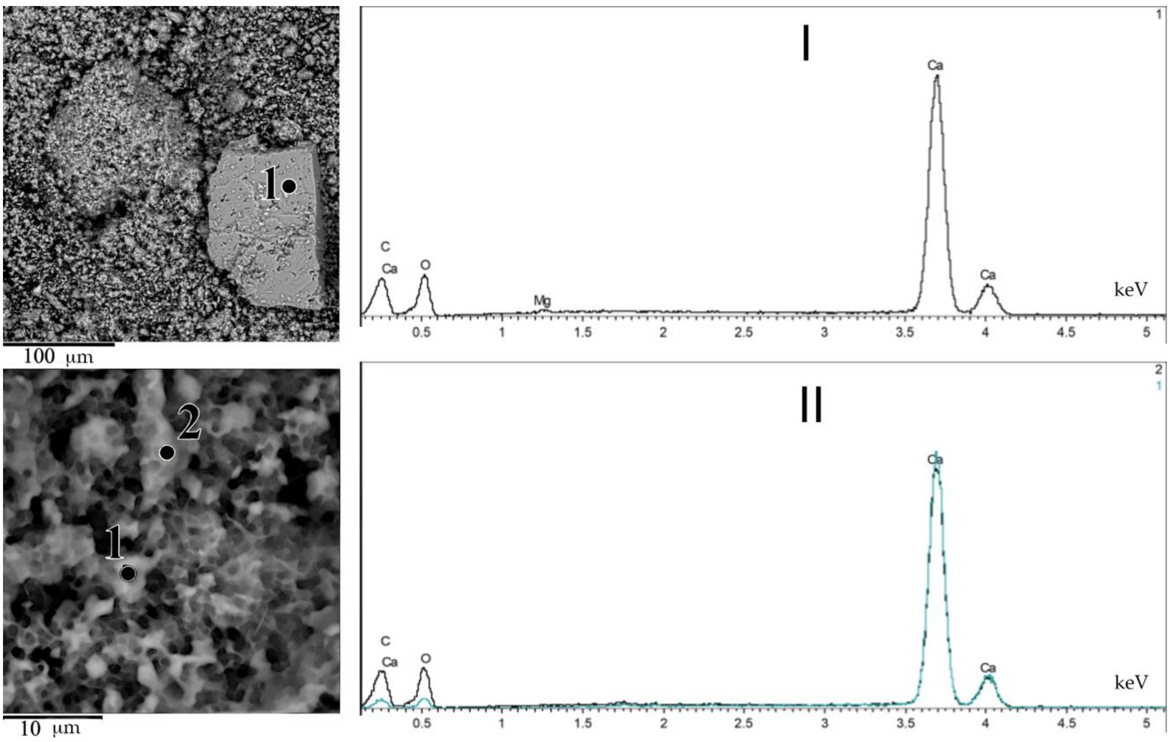


Figure 5. Carbonate masonry material: **I**—calcite aggregates, which are fragments of building materials; **II**—aggregates of microcrystalline mass–recrystallization products; energy spectra (EDX) are shown. Sample E-20-KR-ChU-1.

The difference in the strength properties of large crystalline aggregates and microporous groundmass makes it possible to effectively separate them by means of "soft" grinding of the samples. For this, in the beginning, the existing coarse aggregate (fraction more than 5 mm) was removed from mortar samples, after which the samples were ground with a rubber pestle in a porcelain mortar. This was done so that only the least strong binder mass was destroyed, and the existing fine aggregate, consisting mainly of quartz sand and other rocks, represented mainly with a fraction of more than 0.1 mm, was not crushed. After grinding, the prepared mass was sieved on a sieve with a mesh size of 50 µm for X-ray studies.

This ensures the separation of a fraction less than 50 µm, which contains a minimum amount of primary (natural) calcite and minerals-impurities (quartz, clay, and other aggregates) (examples of the structure of the analyzed aggregates are shown in Figure 6).

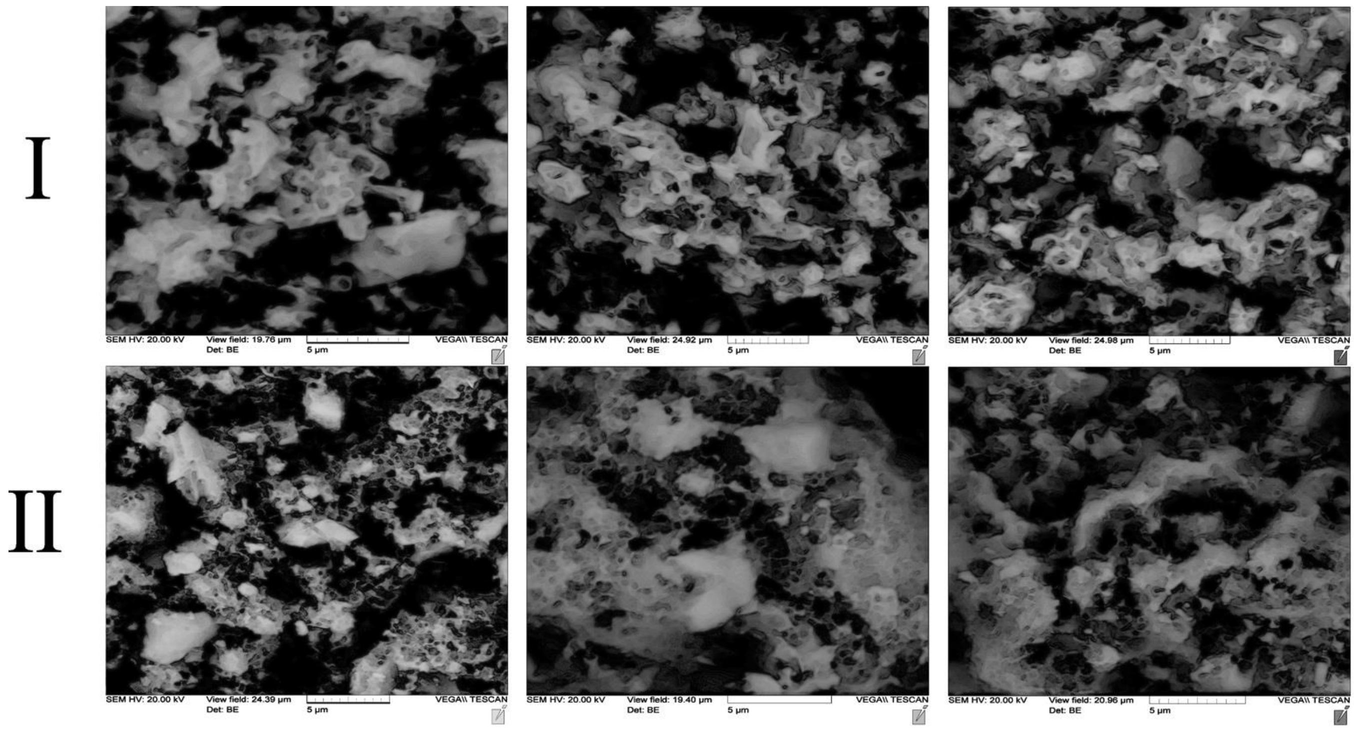


Figure 6. Microstructure of carbonated mortars of Chufutkale buildings (Crimea): **I**—old wall (sample E-20-KR-CHU-1), **II**—tomb (sample E-20-KR-CHU-4).

The isolated fine fraction was studied by powder X-ray phase analysis (Figure 7). At the same time, the analysis of diffraction patterns makes it possible to control the degree of separation of genetically dissimilar calcites additionally. In the presence of a significant amount of natural calcite blocks associated with the material, its most intense reflex (in the region of the angle 2Θ ~ 29.4°) can obtain an asymmetric appearance due to its overlapping with the higher angle region is the peak of magnesium-containing natural carbonate. These samples are excluded from further analysis. For example, Figure 7 shows an X-ray diffraction pattern of a sample, where a small amount of natural primary calcite is present in the form of a filler, as well as other minerals—quartz, mica, clay minerals. Peak's characteristic of portlandite $Ca(OH)_2$ were not found—2.63; 4.93; 1.93; 1.79; 1.69; 3.11 Å.

When interpreting and comparing the results obtained, the confirmed historical data and reference samples with a known age [31] were considered. The studies were carried out on an ARLX'TRA X-ray diffractometer (Thermo Fisher Scientific, Waltham, MA, USA) under the same shooting conditions. All samples prepared for X-ray studies were saved for repeated experiments, and some of the pieces with a confirmed age were saved as reference standards.

The presence in the sample of a significant amount of primary (natural) calcite and other minerals can be easily determined by the X-ray method. In the first case, the most intense calcite peak (at 2Θ ~ 29.4°) acquires a bimodal appearance in the mortar; in the second case, the peaks of the corresponding minerals are clearly visible on the X-ray diffraction patterns. For example, Figure 7 shows an X-ray diffraction pattern of a sample where natural primary calcite is present in a small amount in the form of a filler, which manifests itself in the bimodal appearance of the main calcite peak in the region of angles 2Θ ≈ 29.4°, as well as other minerals—quartz, mica, zeolites, gypsum. Peaks typical for portlandite were missing in the X-ray patterns Ca $(OH)_2$–2.63 (10); 4.93 (5); 1.93 (5); 1.79 (4); 1.69 (3) Å.

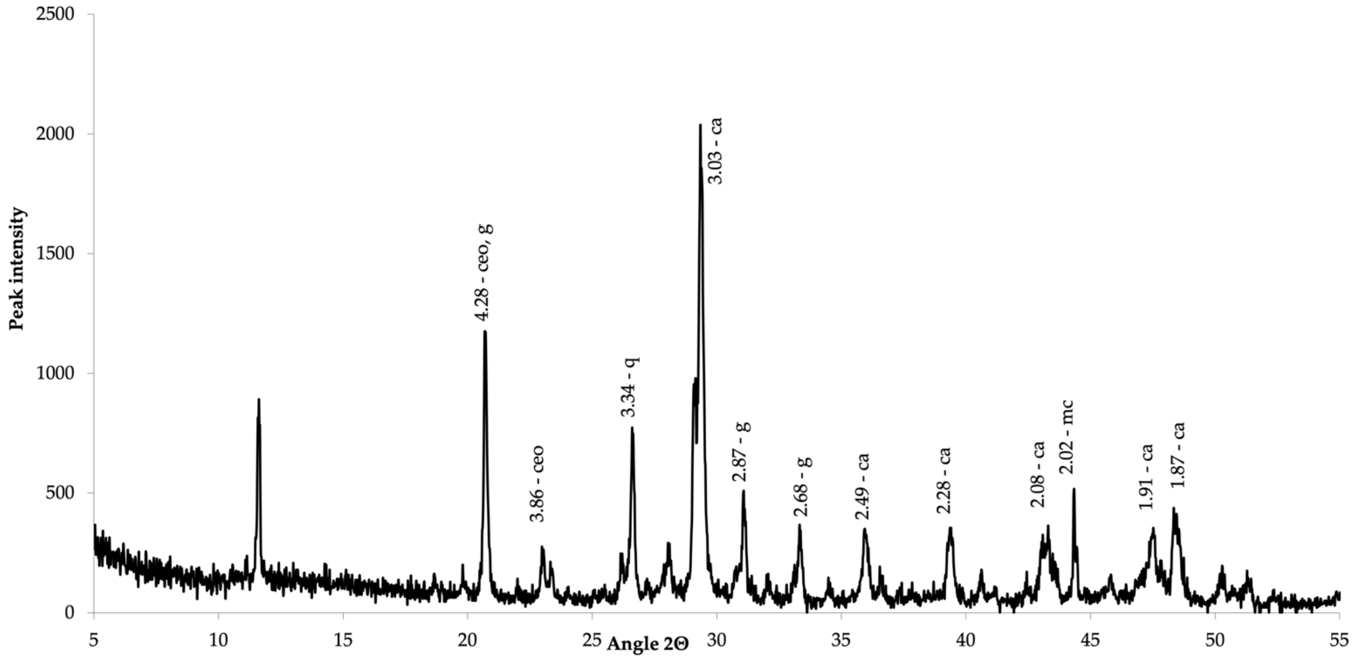
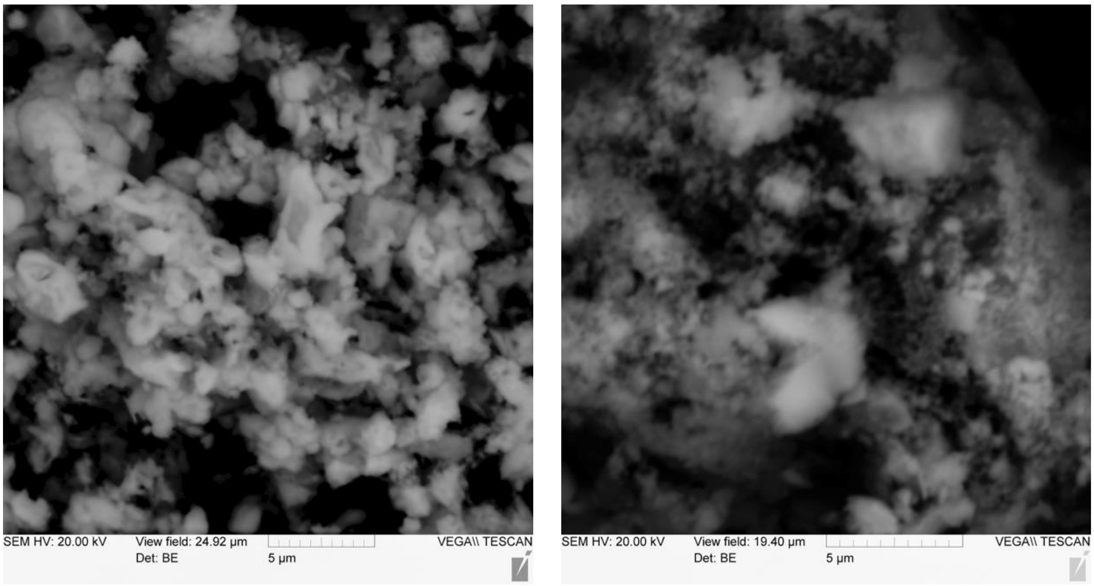


Figure 7. X-ray of a sample from the wall of the Sukhum fortress—Sukhum-kale (architect Yusuf-aga, 1724).

3. Results

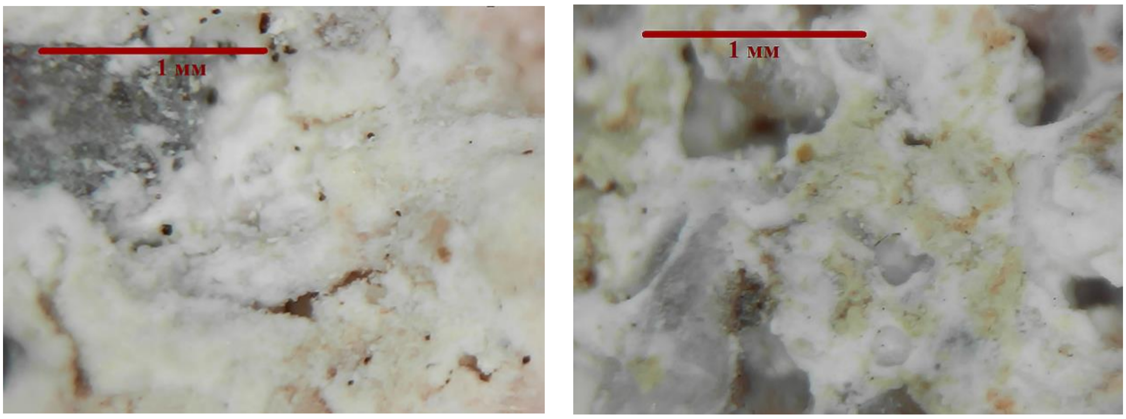
As a result of the studies carried out, it was found that in the samples of lime mortars from buildings of the 18th century and older, the presence of portlandite—$Ca(OH)_2$—was not detected, which manifests itself in the diffraction patterns with peaks corresponding to 2.63; 4.93; 1.93 Å. This is due to its complete transition to calcite. Newly formed calcite has a non-uniform crystalline structure with a predominance of microporous crystal aggregates and their intergrowths less than 5 µm in size (Figure 8a,b).

Under an optical microscope, it is not possible to observe crystallites of secondary calcite. At magnifications of up to 200 times, calcite looks like a chalky, powdery, highly porous mass, although the general background shows that the process of recrystallization is in progress (Figure 9a,b). Other components of the mortar are also observed, the most common of which is quartz sand.



(**a**) (**b**)

Figure 8. Microcrystals of newly formed calcite in lime mortars: (**a**) splicing of calcite microcrystals; (**b**) rare relatively large crystals of calcite.



(**a**) (**b**)

Figure 9. Ancient lime mortars under an optical microscope: (**a**) cryptocrystalline structure of secondary calcite (**b**) calcite between quartz grains.

Studies of natural limestone samples have shown that a higher degree of recrystallization of calcite is regularly observed in marmorized limestone, less in chalk-like limestones (Figures 10 and 11). The main peak of calcite (in the area of angle 2Θ ~ 29.4°) always has a higher intensity under the same shooting conditions than in chalk-like limestones, from which lime was usually obtained. However, in the latter, the degree of recrystallization of calcite and the intensity of the main peak of calcite are always higher than in calcite formed from portlandite.

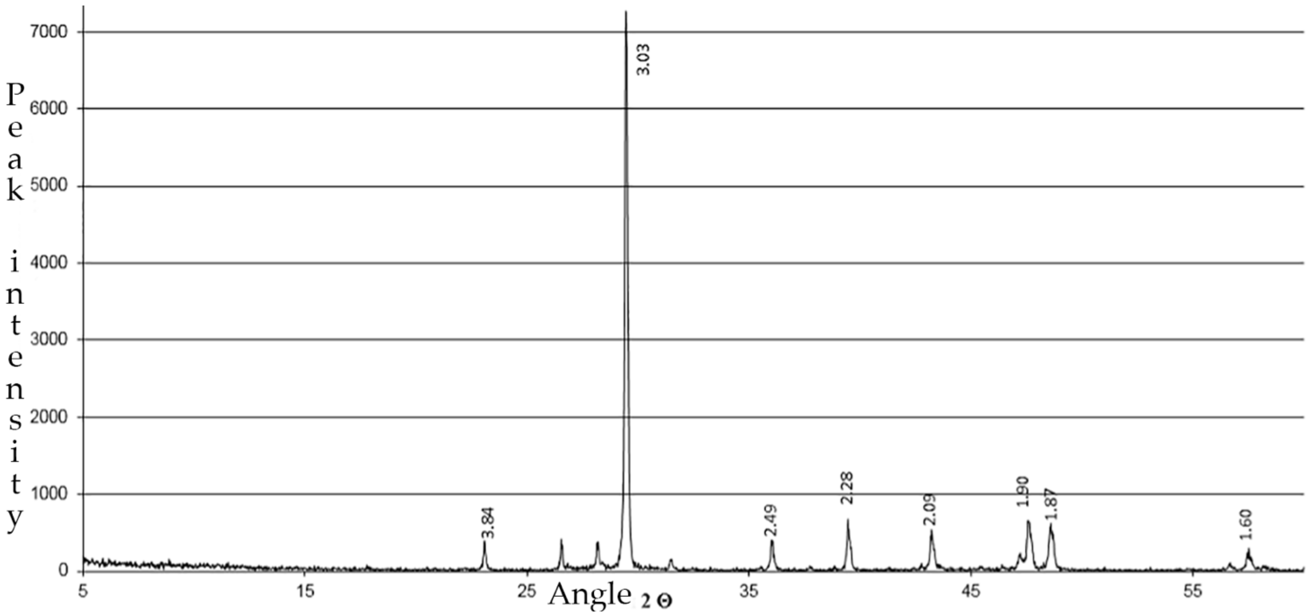


Figure 10. X-ray powder diffraction pattern of marmorized limestone.

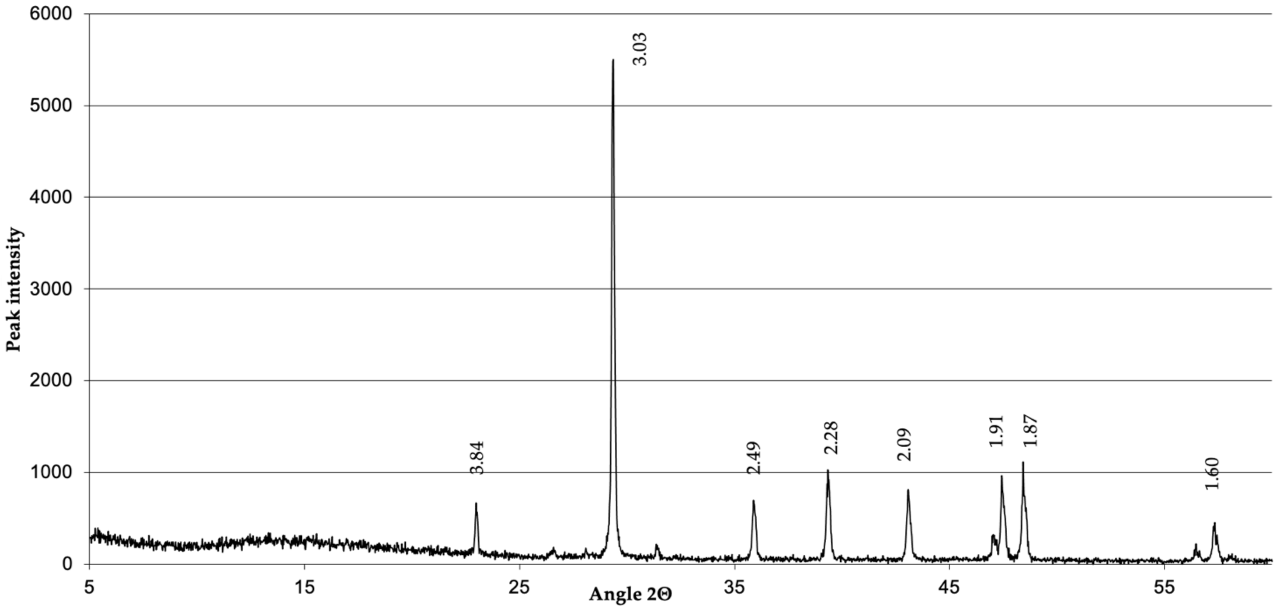


Figure 11. X-ray diffraction pattern of chalk-like limestone sampled near the Anakopia fortress.

The intensity of the main peak of calcite (angle 2Θ ~ 29.4°), a higher crystallinity index (the ratio of the height of the peak to the width at half maximum (FWHM)) and the degree of its recrystallization in older mortars are always higher than in younger ones. Various factors that affect the intensity of the peaks, including the textural orientation of crystallites, the Mg content in calcite, etc. were considered.

For example, Figures 12 and 13 show X-ray diffraction patterns of samples from masonry on a lime mortar in the ancient city of Ephesus (1st century AD) and from the masonry of the gate tower of the Anakopia fortress (10th century AD), which have different ages. The intensity of the calcite main peak (3.03 Å) in the X-ray pattern of mortar from the 1st 339 century AD is one and a half times higher than that of the sample dated at 340 y. of the 10th century AD. There are also other calcite peaks clearly visible, i.e., 1.87; 1.91; 2.09; 2.28; 1.60; 2.49; 3.85 Å.

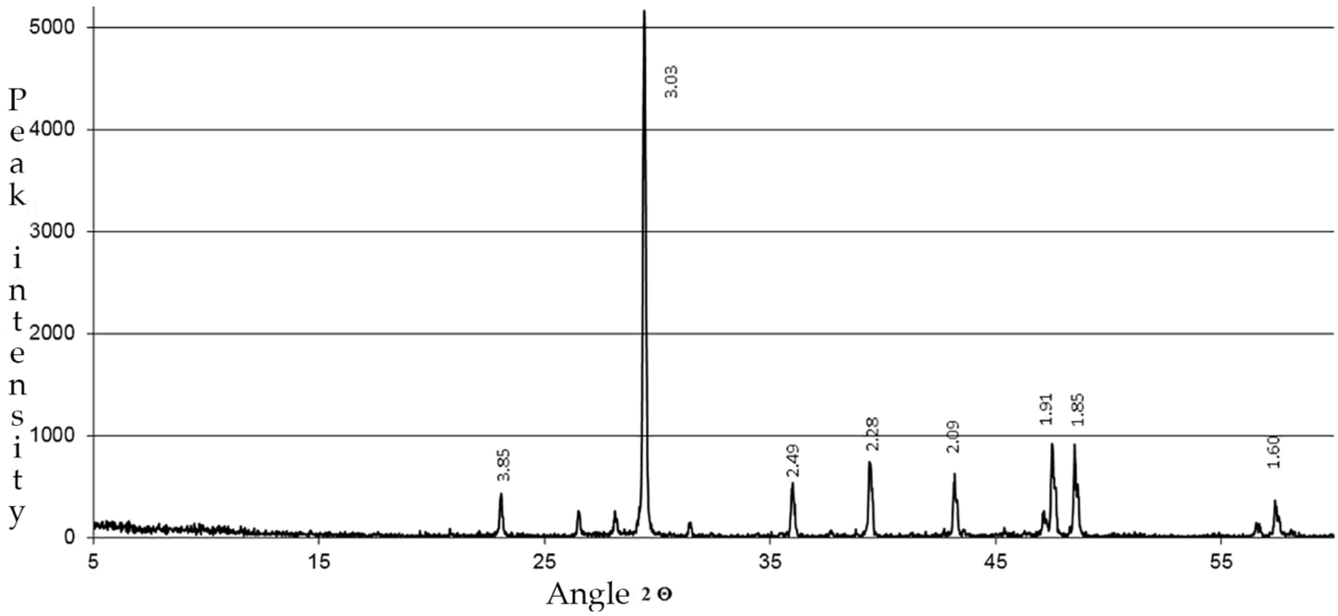


Figure 12. X-ray diffraction pattern of a masonry specimen on a lime mortar in the ancient city of Ephesus (1st century A.D.).

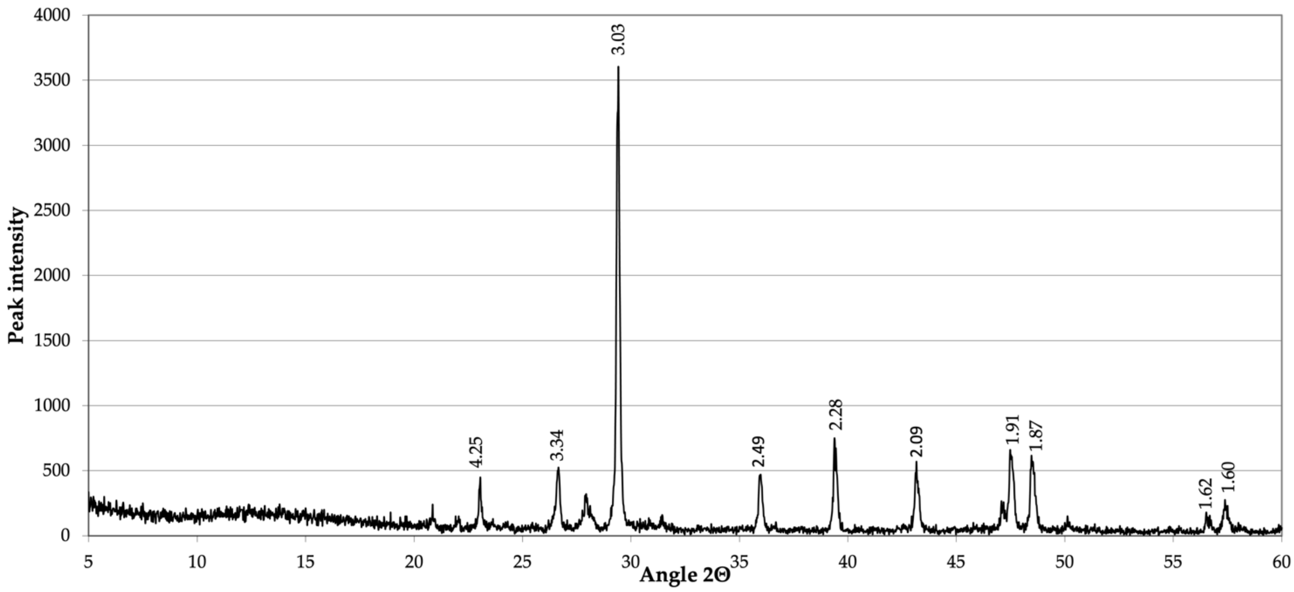


Figure 13. X-ray of a sample from the masonry of the gate tower of the Anakopia fortress (10th century AD).

In the first approximation, to assess variations in the degree of recrystallization of calcite in a series of samples characterizing a local group of objects (areas of masonry structures with signs of repair, different buildings of the same architectural complex, etc.), analysis of line broadening based on an estimate of the ratio of the calcite 104 peak height to its width at half-maximum was used. Analysis of measurements of objects of different ages with known dates showed a high correlation of this value with the age of the clutch known from historical data. An illustration is the statistical processing results by the regression analysis of 68 measurements of samples from the masonry of buildings in Abkhazia, dating from the 10th–17th centuries. The results are shown in Figure 14. Figure 14 shows the dependence of the object's age on the crystallinity index L (the ratio of the peak height to the width at half maximum, dimensionless value).

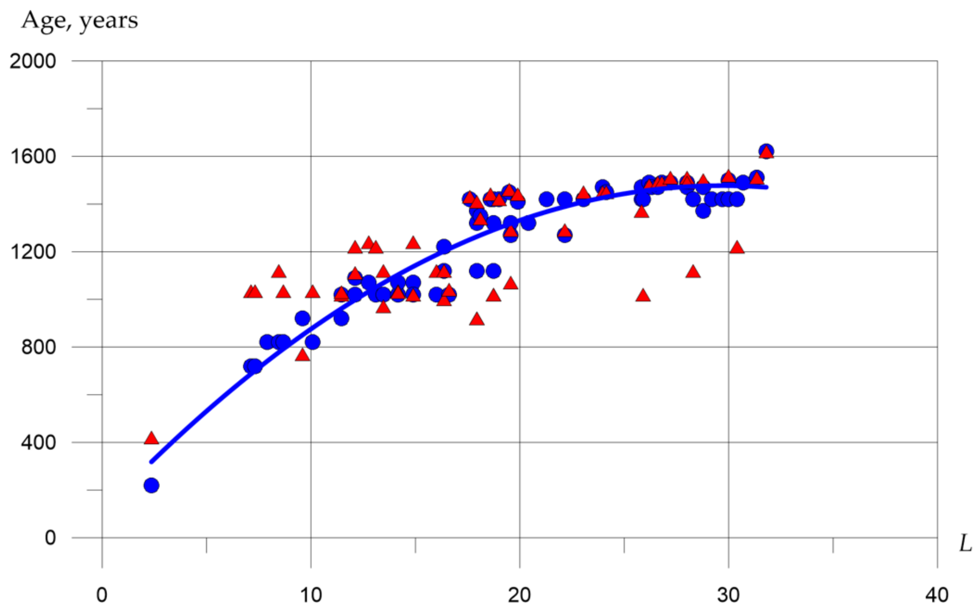


Figure 14. Dependence of the object's age on the crystallinity index *L*. Blue—predicted values according to the authors' method. Red—age of objects from archaeological data.

Figure 15 shows the dependence of the object's age on absolute intensity of the calcite most intense peak H_{max}.

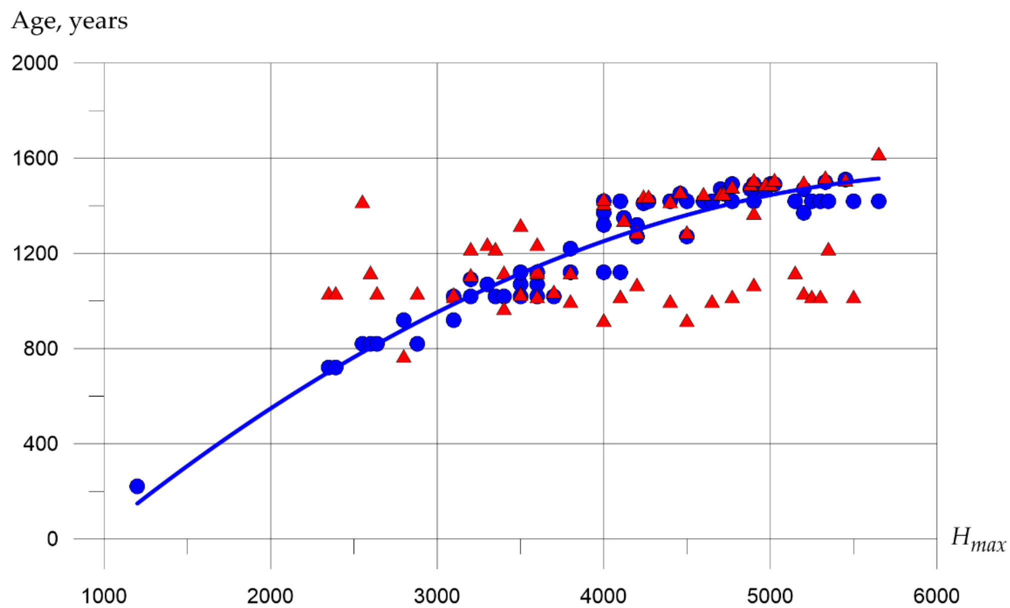


Figure 15. Dependence of the object's age on absolute intensity of the calcite most intense peak H_{max}. Blue—predicted values according to the authors' method. Red—age of objects from archaeological data.

The dependences shown in Figures 14 and 15 were obtained by the least squares method and demonstrate a high correlation. Thus, the coefficient of determination between the crystallinity index *L* and the predicted age is $R = 0.91$. The coefficient of determination between age and peak intensity is 0.92. There is a close correlation between the parameters *L*, the crystallinity index and H_{max} (Figure 16).

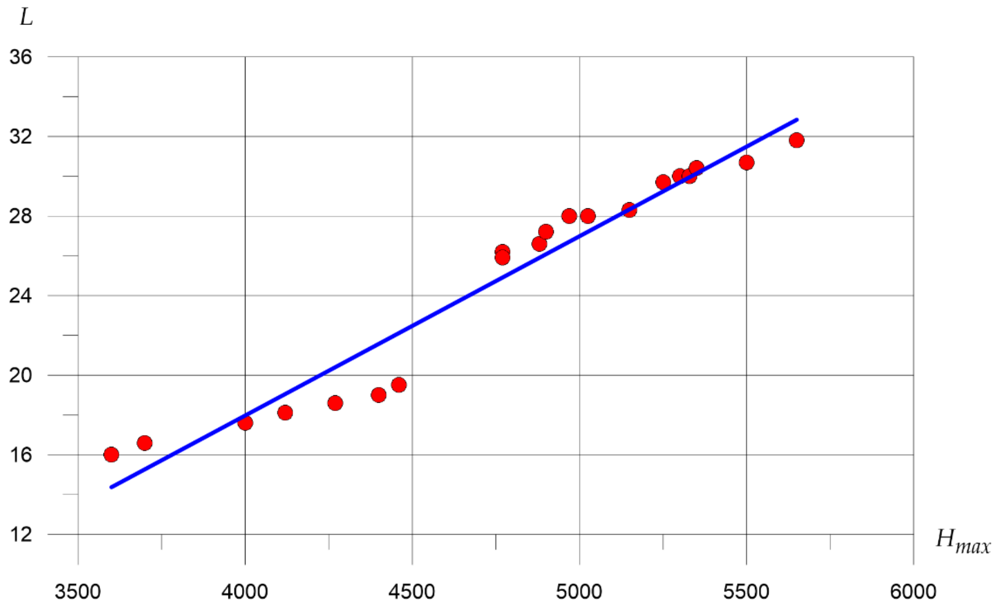


Figure 16. Dependence of the crystallinity index *L* on the absolute intensity of the most intense peak of calcite H_{max}: Red–experimental data; Blue–trend line.

The coefficient of determination for the dependence shown in Figure 16 R = 0.945.

For each group of objects under consideration, a trend of dependence between the specified ratio and the age of mortar is thus established (when measuring a series of samples under uniform conditions). The samples that do not correspond to the age trend established from the samples with known dating require additional research (and when the results are reproduced on duplicates, they can be considered as potentially belonging to the reconstructed sections of the structures). Detailed studies provide for calculations taking into account the background of the crystallinity index for the reflection hkl 104, the measure of which is the full width at half maximum (FWHM). In the process of recrystallization, with an increase in the age of brickworks, the crystallinity of the newly formed calcite increases. An example is the results of studying mortars from the buildings of Chufut-kale (Crimea) of the XI–XIV centuries (Figure 17); for a wall, the construction of which dates back to the XI century, the FWHM value is 0.28–0.30, for buildings in the XIV century, 0.32–0.34.

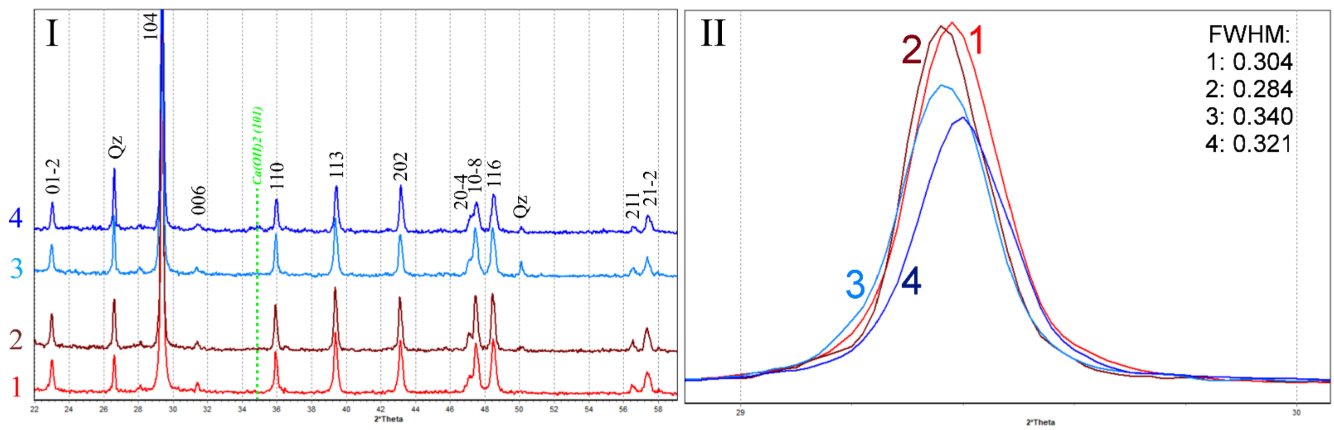


Figure 17. Diffraction patterns of mortars samples from the Chufut-kale (Crimea) structures: **I**—diffractograms of the samples, **II**—the shape of the peaks corresponding to the calcite peak (hkl) 104 calcite. Samples: 1, 2—old wall (sample E-20-KR-CHU-1, E-20-KR-CHU-2), XI century; 3—tomb (sample E-20-KR-CHU-4), 1380; 4—mosque (sample E-20-KR-CHU-5), 1347. Calcite hkl, quartz peaks (Qtz), position of the most intense portlandite reflex (101), FWHM values are indicated.

4. Discussion

Numerous analyses made it possible to establish a clear relationship: the older the object is, and, accordingly, the brick or masonry, confirmed by architectural and archaeological data, the higher the degree of recrystallization of calcite formed from portlandite. It was also established that the rate of crystallization of calcite depends on many conditions, and presumably, in the first centuries, the process is more intensive, and with increasing age, the rate slows down.

The dependencies in Figures 14–16 show a regression relationship between the crystallinity index L and age and the intensity of the peak H_{max} and age. The results in Figures 14–16 are compared with data obtained from archaeological or architectural sources and are in good agreement with the predicted values of the age of the buildings. It should be noted that there is no consensus among archaeologists or architects for many objects; therefore, the proposed methodology will clarify information about the construction time of the object.

The study of ancient lime mortars by the proposed method allows in some cases to confirm, clarify, and in some cases, to determine the age of the objects of architectural heritage and their individual parts. However, to develop a full-fledged methodology, taking into account the complexity and versatility of the tasks, the accumulation of actual data, the selection of reference samples for different regions and, most importantly, the coordinated work of various specialists is required. Despite the fact that active targeted research of mortars began at the beginning of the last century, medieval lime mortars are still extremely poorly studied. The reason for this is, on the one hand, in the small scale of research, and on the other hand, in the fact that dating of objects, and mortars is carried out by different methods and according to different standards. This circumstance often does not allow comparing the results with each other.

Research related to the dating of architectural buildings can take decades due to the complexity of the process. Thus in [34] it is noted that fifteen years of efforts by Cecil L. Striker and Y. Dogan Kuban have produced impressive results, providing a reliable chronology and identity of the Byzantine building and returning the mosque to an attractive and functional state. The project also offered many new testimonies to the history of Byzantine art and architecture.

Similar studies were conducted in [35–37] for the historical analysis of the ancient Byzantine monument of the Column of Constantine, built in 324–330 AD. The column, originally topped with a colossal gilded bronze statue of Constantine, would have been one of the most notable monuments in the city and one that served to identify the city with the emperor.

In the known studies, including [36–39], great work was made in terms of determining the structure and properties of mortars. However, the authors did not connect to the age of mortars when studying them and, accordingly, the age of cultural heritage objects. The proposed method is unique in its own way since it aims to establish the age of lime mortars within 2000 years.

Studies of the fine fraction of lime mortars of cultural heritage objects, including diffraction studies of microcrystalline calcite aggregates, indicate the prospects of these developments for dating cultural heritage objects and identifying areas of different age in brick and masonry. This method can be an excellent addition to the existing methods for determining the age of architectural heritage monuments. According to the degree of recrystallization of calcite, the assumptions of researchers of the history of architecture about the existence of several construction stages on some objects were confirmed on some of the objects studied by us.

5. Conclusions

The phenomenon of the transformation of portlandite into calcite and the subsequent recrystallization of calcite can be used to assess the age of ancient calcareous masonry for a local group of objects. Diffraction studies of powder samples show a change in the parameters of the main reflection of calcite (hkl 104), which is determined by an increase in the crystallinity of calcite with time. In the presence of a series of samples with a known historical age for a group of objects, a trend is estimated between the parameters of the considered diffraction maximum and the building's age, which makes it possible to use this dependence to determine the age of the studied objects. The reliability of the results obtained is largely determined by the quality of the preparation of analytical samples. The allocation of aggregates of microcrystalline (less than 50 microns) newly formed calcite is provided by "soft" attrition of the solution, this provides the allocation of a looser and less durable than fragments of natural limestone, secondary calcite. Electron microscopy and EDX are effective tools for the quality control of analytical samples.

At the current level of development, the method under discussion makes it possible, when using calibration standards with known age, to determine the relative age within a group of objects of the same region, to identify fragments of masonry restored during the reconstruction of buildings. Compilation between distant objects requires taking into account a number of factors (characteristics of raw materials, climatic conditions, etc.) that affect the processes of recrystallization.

The proposed method for determining and clarifying the age of objects of architectural heritage by the degree of recrystallization of calcite of ancient lime-based mortars makes it possible to supplement and clarify the data of historiography and architecture studies by the age of architectural buildings since most of the monuments lack construction inscriptions and evidence different sources. For individual objects, it was possible to determine the historical stages of construction [6,7].

Author Contributions: Conceptualization, V.K., V.P., and A.N.B.; methodology, V.K. and V.P.; software, A.N.B., I.E., and Y.P.; validation, V.K., V.P., and A.N.B.; formal analysis, V.K., V.P., Y.P., I.E., and A.B; investigation, V.K., V.P., and A.N.B.; resources, B.M., Y.P., and I.E.; data curation, V.K., V.P., and A.N.B.; writing—original draft preparation, V.K., V.P., and A.N.B.; writing—review and editing, V.K., V.P., and A.N.B.; visualization, V.K., V.P., and A.N.B.; supervision, B.M., I.E., V.K., V.P., and A.N.B.; project administration, B.M., V.K., and V.P.; funding acquisition, B.M. and V.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Russian Foundation for Fundamental Research, grant number 19-012-00402\21.

Conflicts of Interest: The authors declare no conflict of interest.

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