New chronology of medieval objects in the Northern Black Sea region according to the method of determining calcite main peak intensity

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Abstract. Determining the ancient architectural and cultural monuments’ age is an important scientific problem. The article presents the results of the ancient brickwork lime mortars study. The portlandite transformation mechanism, which initially constitutes the basis of lime mortar, into calcite is shown. It has been established that this process takes from 100 to 200 years under natural conditions and the speed of this process is influenced by temperature, humidity, peculiarities of interaction with carbon dioxide contained in the air, etc. The examples showing that portlandite is completely transformed into calcite in masonry mortars of the 18th century, and that portlandite has not been found in older mortars are given. It was determined that after portlandite transition to calcite with increasing age, an increase in the calcitere crystallization degree is observed and this is manifested in a higher intensity of calcite peaks (especially the main peak 3.03 Å), increase in the crystallinity index - the width of the peak at half maximum (FWHM) or the main peak integral width, that is, the ratio of the area to the height of the peak above the background. Factual data, which show that in older lime solutions the degree of recrystallization of calcite is higher than in younger ones, are presented. This moment makes it possible to indirectly determine the relative age of brick and masonry of various monuments with architectural heritage, which is especially relevant for the South of Russia, where the objects have been preserved using lime mortars of the northern provinces in the Byzantine ecumene and other periods of various cultures.

1 Discussion

A. Grazzini, [1] applied the non-destructive methods to study the characteristics of historical stone and brickwork without compromising the artistic value of the monumental building. He used sound tests to characterize the stone walls at the Sanctuary of Santa Maria delle Grazie in Varoni, which revealed the texture and structural features of the masonry, and also confirmed the ineffectiveness of strengthening it with mortar injections.

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The problem of estimating the age of lime solutions affects not only historical and cultural aspects, but also archaeological ones, since organogenic limes tones with various calcite fossils were often used to obtain them. Falkenberg, J et al. [2] in his research presented evidence of the widespread use of organogenic limes tones for the lime solutions production and indirect signs of determining their age. Daugbjerg T. S. et al. [3] used radiocarbon dating techniques for historic stone structures containing organic remains. They presented sampling methods for radiocarbon dating of mortars. The authors showed that the samples of ancient mortars can contain various types of organic residues and, accordingly, carbon, which complicates correct testing and can lead to inconclusive results even when using modern methods.

Dating is especially important for specialists in the history of architecture, archaeologists, and historians. Knowing the absolute or even relative age of ancient building objects, specialists can draw many reliable conclusions in their fields of knowledge. Pishchulina V. et al. [4, 5] carried out a comprehensive research on the medieval lime mortars study using chemical, petrographic and X-ray phase analyzes. They investigated lime mortars of ancient buildings in the south of Russia, Armenia, Georgia, Greece, Turkey, Abkhazia and other regions. The results of the analyzes confirmed the estimated dates of the foundation of the second line, for example, of defense of the Anakopia fortress within 570-580 years, the reconstruction of the gate tower in 910-930 and the entrance gate - 950. Analysis of the lime mortars of the church near Anakopia (Akuakh temple) gave the construction time of 650-680 years. The method proposed by the authors for determining and clarifying the age of brick and masonry using 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 archeology, there are many direct and indirect methods for determining the age of certain ancient building objects:
- historical and architectural methods: (Sanjurjo-Sánchez J [6], Batt C. [7]) calendar, typological, stratigraphic dating, serialization, etc.;
- physical and chemical methods (Mattinson, J [8], Thomsen, K.J. [9]): thermo-luminescent method, electron paramagnetic resonance method, dating by remanent magnetization, by racemization of amino acids, radiometric, potassium-argon dating, etc.

Aluker N. et al. in [10] investigated the possibility of using the thermo-luminescent method for dating fossilized paleontological remains of animals. The authors note a relatively simple application and a wide range of chronological periods during which the method gives reliable results with minimal errors. Using the thermo-luminescent method, the authors determined the different ages of the studied mammoth remains: from 12 to 100 thousand years. However, it is known that the thermo-luminescent method works well over long time intervals (Goedicke et al. [11]) and leads to large errors in small ones - for an age of up to 1000 years, the method leads to significant errors.

The radiocarbon method of dating organic remains by measuring the content of the radioactive isotope in the material is now widespread$^{14}$C in relation to stable isotopes of carbon. Baydoun R. et al. [12] investigated the changes in atmospheric CO₂as a result of anthropogenic activities. We analyzed the samples of evergreen and deciduous treesleaves, as well as the seasonal leaves of small plants in the areas of industrial facilities with a CO₂. The data showed that the concentration $^{14}$C in the studied areas was significantly lower due to the release of anthropogenic CO₂, than on clean territory.

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 by Marra F. et al. [13]. The authors examined the volcanic rocks used in the mortars of the ancient Rome buildings from the beginning of the second century BC to the early imperial era in order to establish their pyroclastic origin (Pozzolane Rosse). The
key issues in the study of mortars are usually their strength characteristics [14-16], which are determined, among other things, by non-destructive methods [17, 18].

In an article by Giaccone et al. [19] 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. The experimental studies of aging 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 by Fernandez F. et al [20]. They studied the solutions based on lime - metakaolin and hydraulic lime - metakaolin with the addition of nano-TiO₂ and perlite. It has been shown that the solutions with pearlite and nano-TiO₂ are the most effective, which makes them suitable for the preservation of monuments of cultural heritage.

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 by Mignardi S. et al. [21], including polarized light microscopy (PLM), X-ray powder diffraction (XRPD) and scanning electron microscopy combined with energy dispersive spectroscopy (SEM-EDS), was used to characterize objects belonging to 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 solutions were carried out by Pavlik et al. [22]. Their compatibility and effectiveness have been shown for masonry and plastering materials for the historically valuable buildings’ restoration.

The aim of the work carried out by the authors is to develop a method for the relative determination of the brick and masonry objects of cultural heritage age up to 2000 years, based on X-ray phase analysis according to the calcite recrystallization degree in lime solutions.

For the research, the samples of lime mortars were selected at various objects of the architectural heritage of the Northern Black Sea region and Crimea. In total, in the 2020 session, 149 samples. Objects for the research were classified into "reference", for which there are serious architectural studies, and they are dated by researchers, archaeologists and architects, and "controversial", for which there is no accurate and generally accepted dating data. We also studied the samples of natural carbonate rocks located near the sampling sites and from which lime was most likely obtained for solutions.

The results of the study and their correlation with the dating of archaeologists and architects, documentary sources showed that the main determining age of the elements is the intensity of the main peak of calcite, especially the main peak 3.03 Å (in the sight 20 ~29.4).

Several samples of solutions were taken from each object in accordance with the periodization of parts of the building, aboveground and underground parts, and solar illumination. These factors were taken into account due to the fact that, as it is known, the rates of chemical reactions, and accordingly the transformation of portlandite into calcite and its recrystallization, largely depend on temperature and humidity. However, the studies have shown that this only affects the early stage of strengthening the solution - in the first 100 years.

To confirm the method, the degree of calcitene crystallization was also investigated, namely the value crystallinity index - the width of the peak at half maximum (FWHM) or the integral width of the main peak, that is, the area ratio to the height of the peak above the background, and it turned out that in older solutions these indicators are always (100%) higher than in younger.
The processes of portlandite carbonation (Ca(OH)$_2$), which depend on many technological factors: the dispersion of lime particles, the water content of the solution, temperature fluctuations, the concentration of carbon dioxide, as well as the presence of substances that contribute to an increase in the concentration CO$_2$ inside the crystallizing mass were studied to verify the method. For example, by introducing organic materials: milk, blood, decoction of tree bark, etc., as practiced by ancient Russian masters, as well as the carbonization time. The last of the listed factors is decisive at the recrystallization stage, when the environment parameters are fairly uniform, and the change in the content of atmospheric CO$_2$ and seasonal temperature fluctuations can be neglected on the scale of estimates at the decade or century level. Only long-term additional humidification is important, 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 carbonization, the solution can gain strength due to the interaction of calcium hydroxide with reactive types 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. However, all this refers to the earlier stages of "hardening" of the solution. The last and longest stage of the "life" of a lime solution is the stage, conventionally called by us the stage of calcite recrystallization, accompanied by the growth of calcite microcrystals and an increase in the crystal lattice structural ordering degree. And at this stage, as studies have shown, the above-mentioned factors no longer matter.

Considering the above-said, we have developed a method for preparing the samples for X-ray studies, which consists in "soft" grinding of samples, since secondary calcite - the binder mass itself - is the least strong component of the solution, and the separation of a fine fraction (0-50 μm) consisting of secondary calcite. For this, at the beginning, the existing coarse aggregate (fraction more than 5 mm) was removed from the solution 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.

In the process of preparing samples and separating secondary calcite, we tried to achieve the minimum content of other minerals and rocks - quartz, sandstones, ferruginous and other minerals. If carbonate rocks were used as a solution filler, they tried to exclude the ingress of primary (natural) calcite into the sample or to achieve its minimum content. In any case, natural limestone has a significantly higher strength in comparison with a binder mass and a fractional composition of more than 0.1 mm, therefore, it is not difficult to isolate it during sample preparation.

When interpreting and comparing the results obtained, we were guided by the confirmed historical data and reference the samples with a known age [30]. 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 the repeated studies, and some of the samples with a confirmed age were saved as reference standards (Table 1).

### Table 1. List of objects investigated in 2020.

| No | Registration number | Location, object name | Sampling location | The calcite crystallinity main peak intensity (by instrument ARLXTRA) | Average Dated by the main peak intensity of calcite (ARLXTR Adevice) | Common Dating, century |
|----|---------------------|-----------------------|------------------|---------------------------------------------------------------|---------------------------------------------------------------------|------------------------|
In any case, natural limestone has a significantly higher strength in comparison with a binder mass itself. This was done so that only the least strong binder mass was destroyed, and the existing fine fraction (0–5 mm) was removed from the solution. The last and longest stage of the “life” of a lime solution is the stage, conventionally called by us the stage of the solution. The last of this stage of the solution is characterized by the growth of carbon dioxide compounds and the appearance of the activation of the dissolution of carbonates and bicarbonates with carbonic acid and the activation of ion exchanges, which contribute to an increase in the concentration of carbon dioxide, as well as the presence of substances that verify the method.

The last of this stage of the solution is characterized by the growth of carbon dioxide compounds and the appearance of the activation of ion exchanges, which contribute to an increase in the concentration of carbon dioxide, as well as the presence of substances that verify the method. The listed factors are decisive at the stage of the solution can gain strength due to the interaction of factors: the dispersion of lime particles, the water content of the solution, temperature fluctuations, the concentration of carbon dioxide, as well as the presence of substances that verify the method.

| Location, object | Reference standards (Location, object) | α | Intensity (by strength) | Time | Intensity of the main peak (by strength) | Location, object |
|------------------|---------------------------------------|---|------------------------|------|----------------------------------------|------------------|
| Abkhazia 2020    | Standard                               |   |                        |      |                                        |                  |
| 1. EA-20-TS-1    | Tsand-ripsh                            | column | 5200 | 4800 | 5-6 | 6 |
| 2. EA-20-TS-2    | Tsandripsh                            | porch | 3050-2020 | 3150-2019 | 11 | 10 |
| 3. EA-20-TS-3    | Tsandripsh                            | altar | 5000 | 6 | 6 |
| 4. EA-20-TS-4    | Tsandripsh                            | Wall south | 4200 | 7 | 10 |
| 5. EA-20-TS-5    | Tsandripsh                            | Arch | 4700 | 6 | 6 |
| 6. EA-20-MOK-1   | Mokvi                                 | Masonry | 2640 | 12 | 986 |
| 7. EA-20-MOK-2   | Mokvi                                 | Wall outside | 2390 | 13 | 986 |
| 8. EA-20-MOK-3   | Mokvi                                 | Masonry from the door | 3500-2020 | 3050-2019 | 3500 | End 10 | 986 |
| 9. EA-20-MOK-4   | Mokvi                                 | Sea mold temple | 5200 | Beginning | 6 | 986 |
| 10. EA-20-MOK-5  | Mokvi                                 | Outside | 2350 | 13 | 986 |
| 11. EA-20-MOK-9  | Mokvi                                 | At the door | 2880 | 12 | 986 |
| 12. EA-20-Khas-1 | Khashupse                             | Upper tower | 4720 | 6 | 6 |
| 13. EA-20-Khas-3 | Khashupse                             | Temple altar | 5450 | 4800 | Beginning | 6 | 6 |
| 14. EA-20-Khas-4 | Khashupse                             | Tank | 4240 | 7 | 6 |
| 15. EA-20-AbAn-1 | AbaAnta                               | 1 wall west | 4500 | 8 | 8 |
| 16. EA-20-AbAn-2 | AbaAnta                               | 2 wall east | 4200 | 3900 | 8 | 8 |
| 17. EA-20-AbAn-3 | AbaAnta                               | 3 porch | 3600 | 10 | 8 |
| 18. EA-20-AbAn-4 | AbaAnta                               | 4 lining | 3300 | 10 | 8 |
| 19. EA-20-MU-12  | Mussera                               | Building nearby | 4950 | 5-6 | - |
| 20. EA-20-MU-4   | Mussera                               | North porch | 4900 | 4900 | 5-6 | 6-7 |
| 21. EA-20-MU-10  | Mussera                               | Main facade | 4900-2020 | 4750-2019 | 6 | 10 |
| 22. EA-20-MU-3   | Mussera                               | North wall | 4000 | 7 | 6-7 |
| 23. EA-20-MU-8   | Mussera                               | Altar of the northern apse. | 4300 | 7 | - |
| 24. EA-20-MU-11  | Mussera                               | Galery | 4100 | 7 | - |
| 25. EA-20-MU-7   | Mussera                               | Choir coating | 3500 | 10 | - |
| 26. EA-20-MU-9   | Mussera                               | Altar outside | 2500 | 12 | - |
| 27. EA-20-MU-13  | Mussera                               | Western wall with choirs | 3200 | 3300 | 10 | 10 |
| 28. EA-20-MU-5   | Mussera                               | Altar outside | 2500 | 12 | - |
| 29. EA-20-BAGR-1 | Bagrat’s Castle                       | gates | 4400 | 6 | 11 |
| 30. EA-20-      | Bagrat’s Castle                       | 1st stage | 3800 | 9 | 11 |
|   |   |   |   |   |
|---|---|---|---|---|
| 31. | EA-20-BAGR-3 | Bagrat’s Castle | 2nd stage | 2800 |
| 32. | EA-20-LYKHC-1 | Lykhný’s Castle | Upper tier | 3400 |
| 33. | EA-20-LYKHC-2 | Lykhný’s Castle | vault | 4500 |
| 34. | EA-20-LYKHC-3 | Lykhný’s Castle | Lower tier | 3800 |
| 35. | EA-20-LYKHC-4 | Lykhný’s Castle | gate | 3400 |
| 36. | EA-20-LYKII-1 | Lykhny Church | building extension was destroyed | 2600 |
| 37. | EA-20-LYKII-2 | Lykhny Church | Side chapel south | 4000 |
| 38. | EA-20-LYKII-3 | Lykhny Church | Coating inside the columns | 3600 |
| 39. | EA-20-LYKII-4 | Lykhny Church | column | 4100 |
| 40. | E-20 BZ-1 | Bzyb | Tower in front of the temple | 4150-2020 |
| 41. | E-20 BZ-2 | Bzyb | Tower below | 4000 |
| 42. | E-20 BZ-3 | Bzyb | Old temple | 4600-2020 |
| 43. | E-20 BZ-4 | Bzyb | church | 3600-2020 |
| 44. | E-20 BZ-5 | Bzyb | Main gate | 3350 |
| 45. | E-20 BZ-7 | Bzyb | The wall at the gate | 3200 |
| 46. | E-20 SC-1 | Simon the Canaanite | Altar outside | 3100 |
| 47. | E-20 SC-2 | Simon the Canaanite | Cladding outside | 1200 |
| 48. | E-20-AN-1 | Anacopia | Temple at turn 3 aps | 5350 |
| 49. | E-20-AN-2 | Anacopia | The gate at the old tower | 4770 |
| 50. | E-20-AN-3 | Anacopia | Wall near the gate tower | 5500 |
| 51. | E-20-AN-4 | Anacopia | Gate tower 6th century | 5025 |
| 52. | E-20-AN-5 | Anacopia | Temple at turn 1 | 4120 |
| 53. | E-20-AN-6 | Anacopia | The temple is on the territory citadel down | 4770 |
| 54. | E-20-AN-7 | Anacopia | citadel | 4900-2020 |
| 55. | E-20-AN-8 | Anacopia | Tower wall | 4270 |
| 56. | E-20-AN-9 | Anacopia | Tower bottom, lining | 4460 |
| 57. | E-20-AN-12 | Anacopia | Out | 3700 |
| No. | Code       | Location     | Building Description                | Year 1   | Year 2   |
|-----|------------|--------------|-------------------------------------|----------|----------|
| 58  | E-20-AN-13| Anacopia     | Temple with gate figs               | 5300     | Beginning 6 |
| 59  | E-20-AN-17| Anacopia     | Temple top part                     | 5250     | Beginning 6 |
| 60  | E-20-AN-18| Anacopia     | Wall 2 lines                        | 4000     | 6         |
| 61  | E-20-AN-19| Anacopia     | cistern                             | 5650     | Beginning 6 |
| 62  | E-20-AN-20| Anacopia     | Wall with Alkhas                    | 5330     | Beginning 6 |
| 63  | E-20-AN-21| Anacopia     | East tower                          | 4650     | 6         |
| 64  | E-20-AN-22| Anacopia     | from the East                       | 5150     | Beginning 6 |
| 65  | E-20-AN-23| Anacopia     | Temple top vault                    | 3600     | 10        |
| 66  | E-20-AN-24| Anacopia     | Temple upper vault                  | 4400     | 6         |
| 67  | E-20-AN-25| Anacopia     | Temple upper vestibule              | 4880     | Beginning 6 |
| 68  | E-20-AN-10| Anacopia     | Gate tower bottom                   | 4970     | Beginning 6 |
| 69  | E-20-BAM-1| Bambora      | Temple tower bottom                 | 3500-2020 | End 9     |
| 70  | E-20-BAM-2| Bambora      | Temple extreme                      | 2550     | 12        |
| 71  | E-20-BAM-2| Bambora      | Temple average                      | 3500     | Beginning 10 |

**CRIMEA**

| No. | Code       | Location     | Building Description                | Year 1   | Year 2   |
|-----|------------|--------------|-------------------------------------|----------|----------|
| 72  | E-20-CR-TIR-1| Tiritaka    | House of plaster                    | 2100     | 17        |
| 73  | E-20-CR-TIR-2| Tiritaka    | winery                              | 1530     | 18        |
| 74  | E-20-CR-TIR-3| Tiritaka    | house                               | 2700     | 15        |
| 75  | E-20-CR-TIR-4| Tiritaka    | Temple 3cen.                        | 2850     | 15        |
| 76  | E-20-CR-TIR-5| Tiritaka    | House 3 cen.                        | 3000     | 14        |
| 77  | E-20-CR-TIR-6| Tiritaka    | Nymphaeum                           | 4630     | 12        |
| 78  | E-20-CR-CHUF-1| Chufut-Kale| Old wall                            | 4500     | 12        |
| 79  | E-20-CR-CHUF-2| Chufut-kale| Gate                                | 4270     | 12        |
| 80  | E-20-CR-CHUF-3| Chufut-kale| tower                               | 3250     | 14        |
| 81  | E-20-CR-CHUF-4| Chufut-kale| tomb                                | 3800     | 14        |
| 82  | E-20-CR-CHUF-5| Chufut-kale| mosque                              | 3500     | 14        |
| 83  | E-20-CR-AL-3| Alushta     | Second Tower                        | 4300     | 12        |
| 84  | E-20-CR-AL-5| Alushta     | 2 barbican                          | 4100     | 12        |
| 85  | E-20-CR-CHERS-1| Cherso-nesus| Church No. 9                        | 4550     | 9         |
| 86  | E-20-CR-CHERS-2| Cherso-nesus| Basilica on the cliff              | 4470     | 9         |
| 87  | E-20-CR-CHERS-1| Cherso-nesus| Winemaker'                          | 3370     | 15        |
| No. | Code | Description | Material | 1st | 2nd |
|-----|------|-------------|----------|-----|-----|
| 88. | E-20-CR-CHER-4 | Chersonesus House | plastering | 2650 | 16 | 10 |
| 89. | E-20-CR-CHER-5 | Chersonesus Wine maker's house, with bricks | | 3200 | 15 | 4 |
| 90. | E-20-CR-BO-1 | Bogatoye vault | | 3850 | 12 | 13 |
| 91. | E-20-CR-BO-2 | Bogatoye Western wall | | 2900 | 3700 | 12 | 13 |
| 92. | E-20-CR-BO-3 | Bogatoye Native masonry wall | | 3700 | 12 | 13 |
| 93. | E-20-CR-BO-4 | Bogatoye Outer lining | | 3950 | 12 | 13 |
| 94. | E-20-CR-BO-6 | Bogatoye roof | | 3600 | 13 | 13 |
| 95. | E-20-CR-BO-7 | Bogatoye altar | | 4000 | 12 | 13 |
| 96. | E-20-CR-SU-1 | Sudak Central Hall | | 4350 | 11 | 9 |
| 97. | E-20-CR-SU-2 | Sudak Old temple | | 4720 | 10 | 9 |
| 98. | E-20-CR-SU-3 | Sudak North wall | | 4120 | 4800 | 11 | 9 |
| 99. | E-20-CR-SU-4 | Sudak solution | | 4350 | 11 | 9 |
| 100. | E-20-CR-SU-5 | Sudak From a niche | | 4600 | 10 | 9 |
| 101. | E-20-CR-SU-6 | Sudak From the altar | | 5050 | 10 | 9 |
| 102. | E-20-CR-SU-8 | Sudak From the west wall | | 5250 | 10 | 9 |
| 103. | E-20-CR-MP-1 | Morskoye From the west wall | | 4220 | 11 | 15 |
| 104. | E-20-CR-AP-1 | Sudak 12 apostles bottom | | 1950 | 15 | 12 |
| 105. | E-20-CR-AP-2 | Sudak 12 apostles top | | 2900 | 12 | 13 |
| 106. | E-20-CR-IIAP-1 | PartenitBa silica Old part | | 4150 | 11 | 8 |
| 107. | E-20-CR-oct-1 | Old CrimeaSurg Khach walls | | 3400 | 14 | 13 |
| 108. | E-20-CR-oct-2 | Old CrimeaSurg Khach facing | | 4800 | 10 | 13 |
| | | SOCHI | | | | |
| 109. | C-20-KN-1 | KrionNeron Stone with mortar | | 3650 | 10 | 12 |
| 110. | C-20-KN-2 | KrionNeron 1 | | 3500 | 10 | 12 |
| 111. | C-20-KN-3 | KrionNeron 3 | | 3100 | 11 | 12 |
| 112. | C-20-KN-5 | KrionNeron Knocked out of the ground | | 4380 | 8 | 12 |
| 113. | C-20-LO-1 | LOO South portico | | 4070 | 8 | 11 |
| 114. | C-20-LO-2 | LOO South portico | | 4070 | 7 | 10-11 |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 115. | C-20-LO-3 | LOO | From a fallen piece at the entrance | 3570 | 10 | 11 |
| 116. | C-20-LO-4 | LOO | column | 3100 | 11 | 11 |
| 117. | C-20-LO-5 | LOO | Altar | 4050 | 7 | 11 |
| 118. | C-20-KHO-1 | Khosta | Tower No. 1 and the wall | 2550 | 12 | 11 |
| 119. | C-20-KHO-3 | Khosta | Tower 2-2 wall | 3800 | 10 | 14 |
| 120. | C-20-KHO-4 | Khosta | Tower 4 | 4300 | 8 | 15 |
| 121. | C-20-KHO-5 | Khosta | Tower 5 | 4300 | 8 | 15 |
| 122. | C-20-ACH-1 | Achipse | Center tower | 3700 | 10 | 6 |
| 123. | C-20-ACH-2 | Achipse | Center entrance | 4150 | 9 | 6 |
| 124. | C-20-ACH-3 | Achipse | Tower with road entrance | 3350 | 10 | 6 |
| 125. | C-20-ACH-4 | Achipse | Old entrance | 3650 | 10 | 6 |
| 126. | C-20-MA-1 | Mamayka | old | 3650 | 10 | 5 |
| 127. | C-20-MA-2 | Mamayka | lining | 3750 | 10 | 5 |
| 128. | C-20-MA-3 | Mamayka | 2 stage | 3200 | 10 | 5 |
| 129. | C-20-MA-4 | Mamayka | - | 4300 | 6 | 5 |
| 130. | C-20-LB1-1 | Lesnianska Basilica | tower | 4450 | 6 | 6 |
| 131. | C-20-LB1-2 | Lesnianska Basilica | North Apse | 4350 | 6 | 6 |
| 132. | C-20-LB1-3 | Lesnianska Basilica | In the altar | 3800 | 7 | 6 |
| 133. | C-20-LB1-4 | Lesnianska Basilica | lining | 3200 | 10 | 6 |
| 134. | C-20-AKHS-1 | Akhstyr | altar | 3850 | 9 | 13 |
| 135. | C-20-AKHS-2 | Akhstyr | porch | 4200 | 7 | 14 |
| 136. | C-20-AKHS-3 | Akhstyr | Indented solution | 3700 | 10 | 14 |
| 137. | C-20-AKHS-4 | Akhstyr | In the ground | 2300 | 13 | 15 |
| 138. | C-20-MonD-1 | Dragon's mouth monastery | tower | 3950 | 8 | 11 |
| 139. | C-20-MonD-2 | Dragon's mouth monastery | Tower inside | 4100 | 9 | 11 |
| 140. | C-20-MonD-3 | Dragon's mouth monastery | Indented temple entrance | 3500 | 10 | 7 |
| 141. | C-20-MonD-4 | Dragon's mouth monastery | 1 wall | 4050 | 7 | 7 |
| 142. | C-20-MonD-5 | Dragon's mouth monastery | 2 wall | 4050 | 7 | 11 |
| 143. | C-20-MonD-6 | Dragon's mouth monastery | church | 4400 | 6 | 7 |

Mountain part - standards

|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 144. | Sentin | wall | 3350 | 10 | 10 |
### Standards of the last session Abkhazia

| Church          | Support under-ground | Standards of the last session Abkhazia |
|-----------------|----------------------|---------------------------------------|
| 145. Church     | 3400                 | 10                                    |

2 Results

As a result of the studies carried out, it was found that the presence of portlandite was not detected in the samples of lime mortars from the buildings of the 18th century and older – Ca(OH)$_2$, which manifests itself in the diffraction patterns by 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 microns in size. The morphology of calcite crystals is characteristic of this mineral. The dependence of the calcite crystals size on age has not been established.

The degree of calcite recrystallization and its maximum - the main peak 3.03 Å better defined with slow motion radiographs in the sight area 20~29.4. Numerous analyzes made it possible to establish a clear relationship - the higher the age of the object, and, accordingly, the brick or masonry, confirmed by the architectural and archaeological data, the higher the calcite recrystallization degree formed from portlandite. It was also found that the growth of calcite crystallization depends on many conditions and presumably in the first centuries the process is more intensive, and with increasing age the rate slows down.

The study of ancient lime mortars by the proposed method allows in some cases to confirm, clarify, and in some cases to establish the age of monuments of architectural heritage and their individual parts. However, to develop a full-fledged methodology, taking into account the complexity and versatility of the tasks, it is necessary to accumulate actual data, select the reference samples for different regions and, most importantly, the coordinated work of various specialists.

3 Conclusion

Preliminary comparisons made by us showed that for most of the objects (80-85%) the relative age, determined by the calcite recrystallization degree, correlates with the historical age of the objects of the architectural and cultural heritage, derived on the basis of architectural, historical and archaeological research, and for some objects - no. These are mainly objects with controversial dating. However, for such objects, the dating of lime mortars obtained by the authors of the article coincided with the opinion of a number of the researchers on the construction periods of these objects.

Our proposed method for determining and clarifying the age of objects of architectural heritage by the calcite recrystallization degree of ancient lime solutions makes it possible to supplement and clarify the data of historiography and architectural studies by the age of architectural monuments, since most of the monuments lack construction inscriptions and
evidence from written sources. For individual objects, it was possible to determine the historical stages of construction. The data obtained on a number of objects radically change the generally accepted dating and require further clarification.

The phenomenon of portlandite transformation into calcite and subsequent recrystallization of calcite can be used to estimate the age of ancient limestone 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 the increase in the calcite crystallinity over time. In the presence of a number of samples with a known historical age for a group of objects, the tendency between the parameters of the considered diffraction maximum and the building age is estimated, which makes it possible to use this dependence to determine the age of the objects under study. The reliability of the results obtained is largely determined by the analytical samples’ preparation quality.

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