 https://doi.org/10.1051/e3sconf/202128102028

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 CO_2as 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 CO_2. The data showed that the concentration ^{14}C in the studied areas was significantly lower due to the release of anthropogenic CO_2, 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-$TiO_2$and perlite. It has been shown that the solutions with pearlite and nano-$TiO_2$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 Pavlík 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 calcitere 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_2inside 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)	Avera-ge	Dated by the main peak intensity of calcite (ARLXTR Adevice)	Common Dating, century

		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 wal lwest	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 ernporch	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	1st stage	3800		9	11

	BAGR-2	Castle					
31.	EA-20-BAGR-3	Bagrat's Castle	2nd stage	2800		11	13
32.	**EA-20-LYKHC-1**	**Lykhny's Castle**	Upper tier	3400		10	11
33.	EA-20-LYKHC-2	Lykhny's Castle	vault	4500		6	11
34.	EA-20-LYKHC-3	Lykhny's Castle	Lower tier	3800		8	9
35.	EA-20-LYKHC-4	Lykhny's Castle	gate	3400		10	9
36.	**EA-20-LYKH-1**	**Lykhny Church**	building extension was destroyed	2600		12	9
37.	EA-20-LYKH-2	Lykhny Church	Side chapel south	4000	3800	9	11
38.	EA-20-LYKH-3	Lykhny Church	Coating inside the columns	3600		10	11
39.	EA-20-LYKH-5	Lykhny Church	column	4100		9	11
40.	**E-20 BZ-1**	**Bzyb**	Tower in front of the temple	4150-2020 4000-2019		6	10
41.	E-20 BZ-2	Bzyb	Tower below	4000		7	11
42.	E-20 BZ-3	Bzyb	Old temple	4600-2020 4600-2019		Beginning 6	6
43.	E-20 BZ-4	Bzyb	church	3600-2020 3300-2019		End 9-10	10
44.	E-20 BZ-5	Bzyb	Main gate	3350		10	8
45.	E-20 BZ-7	Bzyb	The wall at the gate	3200		10	8
46.	**E-20 SC-1**	**Simon the Canaanite**	Altar outside	3100		End 10	10
47.	E-20 SC-2	Simon the Canaanite	Cladding outside	1200		18	10
48.	**E-20-AN-1**	**Anacopia**	Temple at turn 3 aps	5350		Beginning 6	8
49.	E-20-AN-2	Anacopia	The gate at the old tower	4770		Beginning 6	6
50.	E-20-AN-3	Anacopia	Wall near the gate tower	5500		Beginning 6	10
51.	E-20-AN-4	Anacopia	Gate tower 6th century	5025		Beginning 6	6
52.	E-20-AN-5	Anacopia	Temple at turn 1	4120		7	7
53.	E-20-AN-6	Anacopia	The temple is on the territory citadel down	4770		Beginning 6	10
54.	E-20-AN-7	Anacopia	citadel	4900-2020 4600-2019		Beginning 6	6
55.	E-20-AN-8	Anacopia	Tower wall	4270		End 6	6
56.	E-20-AN-9	Anacopia	Tower 2 bottom, lining	4460		6	6
57.	E-20-AN-12	Anacopia	Out	3700		10	10

			building with gate figs				
58.	E-20-AN-13	Anacopia	Temple chapel	5300		Beginning 6	10
59.	E-20-AN-17	Anacopia	Temple top part	5250		Beginning 6	10
60.	E-20-AN-18	Anacopia	Wall 2 lines	4000		6	6
61.	E-20-AN-19	Anacopia	cistern	5650		Beginning 6	4
62.	E-20-AN-20	Anacopia	Wall with Alkhas	5330		Beginning 6	6
63.	E-20-AN-21	Anacopia	East tower	4650		6	11
64.	E-20-AN-22	Anacopia	from the East	5150		Beginning 6	19
65.	E-20-AN-23	Anacopia	Temple top vault	3600		10	9
66.	E-20-AN-24	Anacopia	Temple upper vestibule	4400		6	6
67.	E-20-AN-25	Anacopia	Temple upper altar	4880		Beginning 6	6
68.	E-20-AN-10	Anacopia	Gate tower bottom	4970		Beginning 6	6
69.	**E-20-BAM-1**	**Bambora**	Temple altar	3500-2020 3700-2019		End 9	9
70.	E-20-BAM-2	Bambora	Temple extreme	2550		12	6
71.	E-20-BAM-2	Bambora	Temple average	3500		Beginning 10	7
		CRIMEA					
72.	**E-20-CR-TIR-1**	**Tiritaka**	House of plaster	2100		17	3
73.	E-20-CR-TIR-2	Tiritaka	winery	1530		18	3
74.	E-20-CR-TIR-3	Tiritaka	house	2700		15	3
75.	E-20-CR-TIR-4	Tiritaka	Temple 3cen.	2850		15	3
76.	E-20-CR-TIR-5	Tiritaka	House 3 cen.	3000		14	3
77.	E-20-CR-TIR-6	Tiritaka	Nymphaeum	4630		12	4
78.	**E-20-CR-CHUF-1**	**Chufut-Kale**	Old wall	4500		12	6
79.	E-20-CR-CHUF-2	Chufut-kale	Gate	4270		12	6
80.	E-20-CR-CHUF-3	Chufut-kale	tower	3250		14	12
81.	E-20-CR-CHUF-4	Chufut-kale	tomb	3800	3300	14	1380
82.	E-20-CR-CHUF-5	Chufut-kale	mosque	3500		14	1347
83.	E-20-CR-AL-3	**Alushta**	Second Tower	4300		12	15
84.	E-20-CR-AL-5	Alushta	2 barbican	4100		12	15
85.	**E-20-CR-CHER-1**	**Cherso-nesus**	Church No. 9	4550		9	6
86.	E-20-CR-CHER-2	Cherso-nesus	Basilica on the cliff	4470		9	6
87.	E-20-CR-	Cherso-	Winemaker'	3370		15	4

	CHER-3	nesus	s house plastering				
88.	E-20-CR-CHER-4	Cherso-nesus	House	2650		16	10
89.	E-20-CR-CHER-5	Cherso-nesus	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-ПАР-1**	**PartenitBasilica**	Old part	4150		11	8
107.	**E-20-CR-oc-1**	**Old CrimeaSurpKhach**	walls	3400		14	13
108.	E-20-CR-oc-2	Old CrimeaSurpKhach	facing	4800		10	13
		SOCHI					
109.	**C-20-KN-1**	**Krion-Neron**	Stone with mortar	3650		10	12
110.	C-20-KN-2	Krion-Neron	1	3500		10	12
111.	C-20-KN-3	Krion-Neron	3	3100		11	12
112.	C-20-KN-5	Krion-Neron	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 1**	tower	4450		6	6
131.	C-20-LB1-2	Lesnianska Basilica 1	North Apse	4350		6	6
132.	C-20-LB1-3	Lesnianska Basilica 1	In the altar	3800		7	6
133.	C-20-LB1-4	Lesnianska Basilica 1	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

		church					
145.		Sentin church	Support under-ground	3400		10	10
	Standards of the last session Abkhazia						
146.	A-2	Anacopia	Gate towerwall	5100-2020 4400-2019		Beginning6	6
147.	A-5	Anacopia	Temple in citadel	4700-2020 4000-2019		Beginning 6	6
148.	A-8	Gerzeul	Tower	3950-2020 3800-2019		6-7	6
149.	A-45	Round Tower / Anacopia	Gate arch	4700-2020 4400-2019		Beginning 6	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 calcitere crystallization 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 calcitere 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 trans formation 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.

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

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