CHARACTERIZATION OF BROWN LAYERS ON FAÇADES OF ARCHAEOLOGICAL BUILDINGS IN SLOVENIA

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Abstract

Brown layers have occurred just below the façade surface of some archaeological buildings. They are a consequence of chemical changes, which can give rise to further destruction. Brown layers and undamaged plaster underneath the brown layers consist of $CaCO_3$, SiO_2, Ca_2SiO_4, $CaMg(CO_3)_2$, silicate minerals containing Ca, Al, Mg, K, Fe, metal hydroxides and sulphates, with some surface bound water. In both layers coordination of Fe^{3+} ions is tetrahedral and octahedral. In brown layers there are more Fe^{3+} ions at octahedral sites and there is an evidence of a change in chemical environment of ferric ions. The difference between brown layers and undamaged plaster underneath the brown layers is in goethite (α-FeOOH) formation. It is microcrystalline and some of the Fe^{3+} ions are substituted by a non magnetic ion, probably Al^{3+}. Iron in oxidation state 2+ is present only in the brown layer of sample ZMV 7. One of the possible ways of its genesis is reduction of Fe^{3+} due to SO_2 present in the air.

Introduction

A change of colour on archaeological objects often agitates restorers and architects because it is aesthetically unattractive and it can also give rise to further destruction of those objects. On some constructions of historical value in Slovenia, built or renewed around year 1910, brown layers just below the facade surface have occurred. Those layers are hard and thin, usually 1-2mm. There are parts where brown colour has entered even further into the interior of the plaster. In the Centre for Restoration of the Republic of Slovenia they have prepared colour studies[1] of samples taken from building facades. Those studies were done by microscopic observations. Since the borderline between brown layers and undamaged plaster beneath is not sharp, they assumed that brown layers were not created by adding a pigment into the external layer of building facades, but are a consequence of chemical changes.

Some of the former investigations[2,3,4] of cements and iron containing material, have shown, that iron could be included into chemical changes of building plaster. D. Hanžel, D. Dimic and D. Lasič studied hydration behaviour of two Yugoslav cements by Mössbauer spectroscopy.[2] According to their investigation cement contains minerals with ferric ions at octahedral and tetrahedral sites in ferrites of brownmillerite-like structure having the generic formula $2CaO{\cdot}(Fe_2O_3)_{1-x}{\cdot}(Al_2O_3)_x$. Spectra of hydrated samples differ from those of nonhydrated samples. This indicates a change in chemical environment of ferric ions during the process of hydration. There is also an evidence that the ferrite phase might take part in the complex cementing action during ageing.

Analysis of thin black layers on building stone[3,4] showed that the layers mainly consist of various iron oxides and iron oxide hydroxides, sulphates, soot and silicate minerals, with smaller amounts of metal, rubber and asphalt particles. In low concentration are present also the organic constituents.

The aim of this investigation was to characterise brown layers formed on building facades. Various techniques including electronic microanalysis, thermogravimetric and differential thermal analysis, X-ray powder analysis, IR and Mössbauer spectroscopy were used to analyse these layers.

The samples

Samples were taken from 4 archaeological buildings in Slovenia. Three of them are placed in Ljubljana (Zmaj bridge-sample ZMV 7, Barrier on river Ljubljanica-sample ZAP 10, Auersperger palace-sample AUE 37), and one in Domžale (Social home Domžale-sample DDD 36). From each of the four buildings one sample was analysed. In each case, a sample of corresponding undamaged plaster underneath the brown layer was collected for comparison.

Brown layers and undamaged plaster were separated by a diamond knife. The knife was used because the material is very hard, and to avoid contamination. For electronic microanalysis samples were prepared in a shape of a flat tile. For all other analyses samples were milled into powder and homogenised.

Instrumental analysis

Electronic microanalyses were done on an electronic microscope JEOL JSM 35, equipped with energy disperse spectrometer Tractor. Thermo gravimetric and differential thermal analyses were taken on a Perkin-Elmer 7 Series Thermal Analysis system in air flow. The heating rate was 5 °C/min. X-ray powder patterns were taken on a Huber Guinier camera 620 (Cu K_{α}). The patterns were compared with standard patterns in the PDF[5] using μPDSM computer program.[6] Infrared spectra were taken on a Perkin-Elmer FT-IR 1720 X spectrometer in nujol matrix in CsI single crystal windows. Mössbauer spectra were measured by using a Wissel constant acceleration spectrometer. The spectra were analysed by a non-linear least squares fitting procedure. Metallic iron was used as a reference for isomer shift parameter as well as for calibration of the velocity scale. The γ-ray source was ^{57}Co in rhodium matrix.

Results

Elemental composition was determined by electronic microanalysis. The surface of the samples is inhomogeneous. Therefore electronic microanalysis was used only as a qualitative analysis. As it is shown in Table 1 the main component in both layers is calcium. Other elements are present in smaller concentration. Sample AUE 37 – undamaged plaster is unsuitable for this investigation because it is in a form of fine dry particles and it was impossible to get it in a shape of a flat tile.

TABLE 1. The results of the electronic microanalysis given in weight percent considering oxides.
a.) brown layer
b.) undamaged plaster underneath the brown layer
1., 2., 3., 4. – different locations of the same sample
Remark: sample AUE 37-b.) is unsuitable for this investigation

	Ca	**Si**	**K**	**Mg**	**Al**	*S*	**Fe**	*Ti*	*P*	**Cl**
DDD 36 a.) 1.	52.26	4.77	19.19	0.09	3.89	12.91	5.68	0.09		
2.	77.61	10.04	4.34	1.09	1.86	1.53	1.89	0.48		
3.	50.80	2.85	0.77	0.53	12.05			1.03		
b.) 1.	67.64	19.47		0.79	4.76	0.29	5.76	0.21		
2.	87.39	6.58		0.46	1.93	1.37	0.87	0.16		
ZMV 7 a.) 1.	5.03	86.47	1.94		2.05		3.30			
2.	80.80	8.09	1.98	1.54	2.48	1.03	1.65			
3.	80.25	6.77	1.45	2.66	1.54	1.23	2.87	0.65	1.28	
4.	73.99	2.25		17.29	0.38	0.85	1.65		0.86	
b.) 1.	2.60	96.47								
2.	70.65	10.57		8.04	4.49	2.15	2.68			
3.	75.39	1.21		21.99						
4.	69.23	18.13	0.98	5.29	2.64	0.72	1.73			
ZAP 10 a.) 1.	80.93	10.82	0.63		1.04	2.92	1.24			0.59
2.	23.76	39.94	4.71		5.22	18.98	5.85	0.47		
3.	44.42	9.98			2.87	39.34	0.31			
b.) 1.	96.52	1.50							0.64	
2.	41.57	40.62	1.28	0.95	5.68	2.10	5.77	0.98		
3.	93.53	2.63	0.70	0.24	0.39	0.85	0.17	0.10		
AUE 37 a.) 1.	74.53	10.51	2.51	1.03	3.07	2.94	4.13			
2.	68.77	12.49	4.28	1.61	3.29	3.54	5.05			
3.	64.34	13.08	6.92	0.90	3.29	3.23	6.99			

Thermo gravimetric and differential thermal analyses gave similar results for all samples as well as for corresponding undamaged plaster underneath. In both cases TG curves show two significant mass losses, one up to 100 °C and another one more intense in the temperature range of 600-900 °C (Figure 1). At these temperatures DTA curves show two corresponding endothermal peaks. In TG curves a slow, continuous weight loss is noticeable in the temperature range of 100-500 °C. TG analysis of samples DDD 36-undamaged plaster (Figure 2) and ZMV 7-undamaged plaster shows another mass loss at temperature 400-450 ^{o}C.

FIGURE 1. TG and DTA analysis of the sample DDD 36 – brown layer

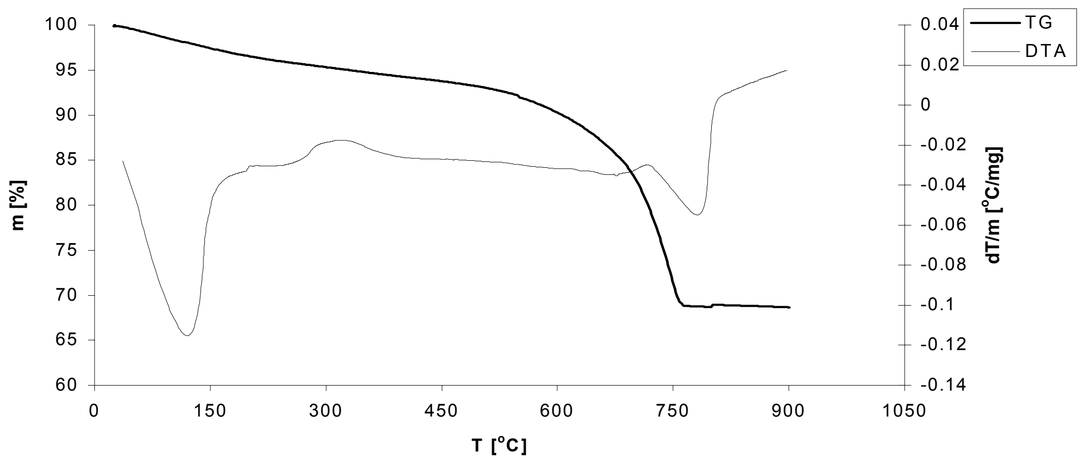
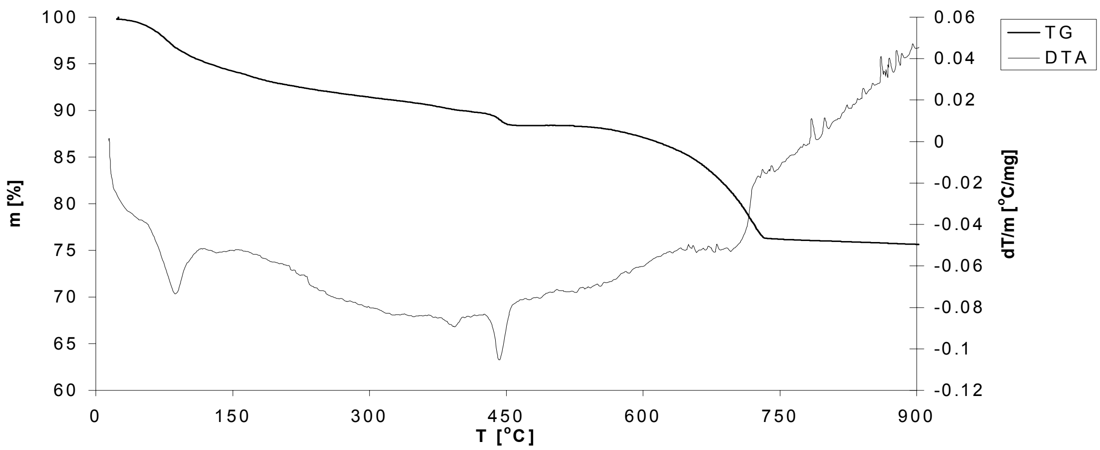


FIGURE 2. TG and DTA analysis of the sample DDD 36 – undamaged plaster underneath the brown



Infrared spectra were taken on a sample DDD 36 – brown layer and on a residual after TG analysis of the same sample. Characteristics:

1. DDD 36 – brown layer
   a.) Broad band in the area of 3700 – 3000 cm^{-1}.
   b.) Strong, broad band ranging from 1500 to 1400 cm^{-1}.
   c.) Broad band in the area of 1200 – 800 cm^{-1} with one sharp peak at 873 cm^{-1}.
   d.) Strong, sharp peak at 713 cm^{-1}.
2. The rest after TG analysis of sample DDD 36 – brown layer
   a.) Sharp band at 3640 cm^{-1}.
   b.) Broad band in the area of 1200 – 800 cm^{-1}.

X-ray powder analyses were done on all samples and on TG residuals. Powder patterns show many broadened or overlapping diffraction lines. It is therefore difficult to determine the exact composition of samples. Components which show the best matching of lines comparing to lines of components from PDF computer database are: $CaCO_3$, SiO_2, Ca_2SiO_4 and $CaMg(CO_3)_2$. It was often easier to determine composition of the rest after TG analysis because the lines are sharper and less overlapping. Tables from 2 to 17 show the results of x-ray powder analysis.

Mössbauer spectra have been recorded on brown layers of samples DDD – 36 and ZMV – 7 and on the undamaged plaster underneath brown layers of these samples. Spectra of undamaged plaster of both samples consist of two overlapping doublet patterns (Figure 3). Similar patterns are present also in spectra of brown layers (Figure 4) except there is a change in quadrupole splitting parameter of approximately 0.2 mm/s and the ratio of relative intensities also becomes different. In the spectrum of sample ZMV – 7-brown layer (Figure 5) another quadrupole splitting doublet is present, with higher values for isomer shift and quadrupole splitting parameter but a very low intensity. Hyperfine parameters of Mössbauer spectra recorded at room temperature are given in Table 18 and 19.

TABLE 2. Diffraction lines (d) and relative intensities (I/I_0) of the sample ZMV 7-brown layer compared to lines of the most probable components from μPDSM computer database. For each compound its mineral name and the number of PDF card are given.

SAMPLE ZMV 7-brown layer		**$CaCO_3$** (Calcite) 5-0586*		**SiO_2** (Quartz) 5-0490D		**Ca_2SiO_4** (Larnite) 33-0302*		**$CaMg(CO_3)_2$** (Dolomite) 36-0426*		**$Ca_2Al_3Si_3O_{15}H_2$** (Zoisite) 13-0562I	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
3.324	90			3.343	214	3.322	89				
3.037	100	3.035	199			3.021	8.9			3.068	19
2.889	80					2.895	4.4	2.888	222	2.874	42
2.778	30					2.775	8.9			2.790	19
2.698	30					2.671	18	2.670	9	2.720	6.4
2.608	10					2.588	4.4				
2.536	10							2.539	7	2.536	6.4
2.494	40	2.495	28							2.516	3.2
2.284	60	2.285	36	2.282	26	2.302	4.4			2.280	6.4
2.236	10					2.242	44				
2.191	50							2.193	42		
2.127	10			2.128	19						
2.111	10									2.101	13
2.096	50	2.095	36								
2.015	10					2.019	4.4	2.015	22	2.019	22
1.977	20			1.980	13	1.982	8.9			1.984	13
1.925	20	1.927	10								
1.910	40	1.913	34			1.912	18				
1.876	40	1.875	34			1.878	35				
1.846	10					1.836	27				
1.816	40			1.817	36						
1.805	10			1.801	2			1.805	22		
1.788	40							1.787	29		
1.604	10	1.604	16	1.608	2					1.601	22
1.541	30			1.541	32			1.545	9	1.541	13
1.525	10	1.525	10								
1.381	10			1.382	15			1.388	4		
1.373	10			1.375	24						

TABLE 3. Diffraction lines (d) and relative intensities (I/I_0) of the sample ZMV 7-undamaged plaster compared to lines of the most probable components from μPDSM computer database. For each compound its mineral name and the number of PDF card are given.

SAMPLE ZMV 7-undamaged plaster		$CaCO_3$ (Calcite) 5-0586*		SiO_2 (Quartz) 5-0490D		Ca_2SiO_4 (Larnite) 33-0302*		$CaMg(CO_3)_2$ (Dolomite) 36-0426*		$Ca_2Al_3Si_3O_{12}(OH)$ (Clinozoisite) 13-0563D	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
3.324	90			3.343	97						
3.037	40	3.035	66			3.049	4.8			3.033	21
2.888	100					2.877	11	2.888	193	2.885	60
2.777	30					2.790	52			2.789	21
2.695	30					2.718	16	2.670	8	2.669	18
2.637	10									2.634	9.6
2.607	10					2.610	23			2.587	18
2.540	10					2.545	4.8	2.539	6		
2.402	30					2.410	7	2.404	14	2.397	12
2.282	10	2.285	12	2.282	12	2.301	2.2			2.300	2.4
2.192	50					2.189	27	2.193	37		
2.105	10	2.095	12			2.103	0.5			2.097	15
2.015	40					2.027	8.1	2.015	19	2.014	4.8
1.929	10	1.927	3.3								
1.905	10	1.913	11			1.912	3.2				
1.817	30			1.817	16	1.821	1.6			1.813	6.0
1.802	10					1.805	4.8	1.805	19		
1.785	30					1.790	3.8	1.787	25		
1.525	10	1.525	3.3								
1.381	10			1.382	6.8			1.388	4		
1.373	10			1.375	11						

TABLE 4. Diffraction lines (d) and relative intensities (I/I_0) of the rest after TG analysis of the sample ZMV 7-brown layer compared to lines of the most probable components from µPDSM computer database. For each compound its mineral name and the number of PDF card are given.

The rest after TG ZMV 7-brown layer		**CaO** (Lime) 43-1001D		**SiO_2** (Quartz) 5-0490D		**Ca_2SiO_4** (Larnite) 24-0037D		**$Ca_{54}MgAl_2Si_{16}O_{90}$** 13-0272		**$CaFe_3O_5$** 30-0256		**$CaSO_4$** (Anhydrite) 6-0226D		**Mg_2SiO_4** 34-0556	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
4.238	20			4.260	81	1.264	4.8								
3.485	40											3.498	111	3.460	4.1
3.330	100			3.343	230			3.039	35					3.340	8.3
3.178	40					3.175	4.8			3.210	5			3.210	33
3.109	10											3.118	4		
3.029	10					3.048	11								
2.997	10							2.973	14						
2.965	10							2.968	14						
2.884	10					2.878	23								
2.841	10					2.841	17					2.849	39	2.850	17
2.795	10					2.793	86	2.776	71	2.810	27	2.797	4		
2.769	70	2.777	17			2.748	95	2.764	42			2.473	9		
2.741	70					2.732	49	2.748	28						
2.689	60					2.717	94							2.680	33
2.662	30									2.660	109				
2.625	40					2.610	74	2.606		2.620	33			2.620	41
2.598	40					2.582	18	2.608	50						
2.505	10					2.503	12			2.490	27			2.510	17
2.471	10					2.493	26							2.480	17
2.449	40			2.458	28	2.452	2.9							2.440	83
2.396	50	2.405	46							2.390	11				
2.320	10					2.305	17	2.323	7.1			2.328	22		
2.276	50			2.282	28	2.282	35							2.270	4.1
2.229	20			2.237	14					2.240	16			2.230	17
2.200	40					2.189	61	2.184	28	2.200	60	2.208	22	2.200	33
2.183	40					2.166	10	2.180	28			2.183	9		
2.119	50			2.128	21	2.132	2.9								

TABLE 4 CONTINUE

The rest after TG ZMV 7-brown layer		**CaO** (Lime) 43-1001D		**SiO_2** (Quartz) 5-0490D		**Ca_2SiO_4** (Larnite) 24-0037D		**$Ca_{54}MgAl_2Si_{16}O_{90}$** 13-0272		**$CaFe_3O_5$** 30-0256		**$CaSO_4$** (Anhydrite) 6-0226D		**Mg_2SiO_4** 34-0556	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
2.100	70					2.106	18			2.107	71	2.086	11		
2.043	20					2.047	20								
2.020	20					2.026	5.7							2.020	83
1.978	10			1.980	14	1.984	22	1.977	7.1	1.973	27	1.993	7		
1.968	10							1.983	7.1						
1.938	30							1.938	7.1	1.933	9	1.938	4	1.940	4.1
1.923	30					1.913	5.7	1.923	7.1						
1.901	10					1.894	28			1.897	3			1.910	8.3
1.834	10					1.847	5.7	1.824	7.1						
1.814	70			1.817	39	1.821	4.8	1.823	7.1					1.820	1.7
1.798	20			1.801	2	1.809	17								
1.790	20					1.791	11								
1.767	10					1.767	10	1.766	28					1.760	12
1.751	10					1.762	6.7	1.761	28			1.749	13	1.740	8.3
1.696	30	1.701	23			1.707	14			1.699	21				
1.687	30														
1.644	10					1.635	7.6			1.650	3	1.648	15	1.640	8.3
1.628	20					1.628	8.6	1.629	7.1						
1.573	10									1.581	2			1.570	1.7
1.565	10											1.564	7	1.560	8.3
1.541	30			1.541	35			1.541	7.1	1.546	20			1.541	17
1.499	50									1.508	10				
1.490	10							1.490	14			1.490	7		
1.486	50							1.488	14						
1.463	10							1.465	7.1	1.469	22				
1.455	10			1.453	7			1.459	7.1						
1.449	10	1.450	6												
1.381	10	1.389	6	1.382	10										
1.373	10			1.375	25										
1.370	40			1.372	21							1.365	2		
1.255	20			1.255	9										

TABLE 4 CONTINUE

The rest after TG ZMV 7-brown layer		CaO (Lime) 43-1001D		SiO_2 (Quartz) 5-0490D		Ca_2SiO_4 (Larnite) 24-0037D		$Ca_{54}MgAl_2Si_{16}O_{90}$ 13-0272		$CaFe_3O_5$ 30-0256		$CaSO_4$ (Anhydrite) 6-0226D		Mg_2SiO_4 34-0556	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
1.238	10											1.237	2		
1.227	30			1.228	5										
1.214	10											1.216	4		
1.204	10	1.203	2.3	1.200	12										
1.183	10			1.184	9							1.199	2		
1.179	10			1.180	9							1.178	1		
1.162	10											1.166	4		

TABLE 5. Diffraction lines (d) and relative intensities (I/I_0) of the rest after TG analysis of the sample ZMV 7-undamaged plaster compared to lines of the most probable components from µPDSM computer database. For each compound its mineral name and the number of PDF card are given.

The rest after TG ZMV 7-undamaged plaster		CaO (Lime) 43-1001D		SiO_2 (Quartz) 5-0490D		Ca_2SiO_4 (Larnite) 9-0351D		$Mg_3Al_2Si_3O_{12}$ 30-0788O		MgO (Periclase) 43-1022C		$Ca_2(Al,Fe)_2O_5$ (Brownmillerite) 30-0226*		$Ca_3Al_2O_6$ 32-0150*	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
4.905	30					4.900	12								
4.406	10							4.460	4.3					4.409	3.4
4.259	20			4.260	56									4.215	2.4
3.493	10							3.510	73						
3.346	90			3.343	159	3.377	15							3.352	2.4
3.269	20					3.241	17								
3.137	10					3.175	15								
3.117	10													3.128	0.5
3.074	10					3.046	17							3.055	3.4
2.886	20					2.876	43								
2.827	70					2.814	25							2.816	1.9
2.782	70	2.777	35			2.795	124					2.784	14		
2.753	100					2.780	112								
2.731	20					2.744	118							2.714	31
2.696	90					2.716	50					2.673	19	2.693	48
2.668	40														

TABLE 5 CONTINUE

The rest after TG ZMV 7-undamaged plaster		**CaO** (Lime) 43-1001D		**SiO_2** (Quartz) 5-0490D		**Ca_2SiO_4** (Larnite) 9-0351D		**$Mg_3Al_2Si_3O_{12}$** 30-0788O		**MgO** (Periclase) 43-1022C		**$Ca_2(Al,Fe)_2O_5$** (Brownmillerite) 30-0226*		**$Ca_3Al_2O_6$** 32-0150*	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
2.640	60											2.644	54		
2.608	60					2.608	81	2.592	81						
2.455	30			2.458	19	2.453	25	2.440	13	2.432	7.9	2.472	1.1		
2.399	70	2.405	95			2.407	25	2.380	34						
2.236	10			2.237	10										
2.201	50													2.206	9.6
2.192	50					2.196	15							2.186	1.9
2.126	30			2.128	14	2.130	15								
2.106	60					2.099	110	2.097	86	2.106	73	2.210	4.3		
2.049	20					2.048	25					2.051	19	2.048	1.0
2.040	20					2.041	15							2.032	1.0
1.998	80					1.983	43								
1.980	10			1.980	10										
1.966	10													1.963	1.4
1.938	50														
1.928	20							1.930	4.3			1.928	19	1.919	17
1.908	20					1.913	12							1.906	1.4
1.819	40			1.817	27	1.821	7					1.815	24	1.828	0.5
1.803	40			1.801	2	1.808	15								
1.791	40					1.791	15					1.795	1.6	1.797	0.5
1.768	30					1.768	7							1.768	0.5
1.757	30							1.752	34						
1.699	50	1.701	47			1.707	17							1.699	0.5
1.691	30														
1.672	10			1.672	11										
1.655	10			1.659	5	1.661	5								
1.629	50					1.634	17	1.623	77					1.625	1.4
1.575	10					1.575	15					1.578	7.6	1.564	17
1.555	10					1.552	12	1.546	4.3			1.564	2.2	1.551	9.6
1.541	30			1.541	24							1.538	7.6		
1.504	10											1.501	4.3		

TABLE 5 CONTINUE

The rest after TG ZMV 7-undamaged plaster		CaO (Lime) 43-1001D		SiO_2 (Quartz) 5-0490D		Ca_2SiO_4 (Larnite) 9-0351D		$Mg_3Al_2Si_3O_{12}$ 30-0788O		MgO (Periclase) 43-1022C		$Ca_2(Al,Fe)_2O_5$ (Brownmillerite) 30-0226*		$Ca_3Al_2O_6$ 32-0150*	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
1.489	50					1.485	10			1.490	37			1.493	1.4
1.411	10			1.418	2	1.417	12	1.410	30					1.414	0.5
1.392	10	1.389	12			1.397	7	1.392	4.3			1.390	3.2		
1.383	10			1.382	11										
1.375	10			1.375	18			1.373	39						
1.349	10													1.347	5.8
1.272	10							1.269	4.3	1.270	4.3				
1.262	40			1.256	6			1.258	4.3						
1.216	10									1.216	11				
1.200	30	1.203	4.8	1.200	8										
1.152	40			1.153	3										

TABLE 6. Diffraction lines (d) and relative intensities (I/I_0) of sample DDD 36-brown layer compared to lines of the most probable components from μPDSM computer database. For each compound its mineral name and the number of PDF card are given.

SAMPLE DDD 36-brown layer		$CaCO_3$ (Calcite) 5-0586*		CaO (Lime) 28-0775	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
4.1511	30				
3.8619	10	3.86	21		
3.3408	30			3.33	69
3.0260	100	3.035	171	3.00	69
2.4837	30	2.495	24		
2.2774	50	2.285	31	2.28	41
2.0894	40	2.095	31	2.09	28
1.9061	40	1.913	29	1.91	41
1.8701	40	1.875	29	1.88	41

Remark: The presence of CaO is questionable.

TABLE 7. Diffraction lines (d) and relative intensities (I/I_0) of sample DDD 36-undamaged plaster compared to lines of the most probable components from µPDSM computer database. For each compound its mineral name and the number of PDF card are given.

SAMPLE DDD 36- undamaged plaster		**$CaCO_3$** (Calcite) 5-0586*		**Ca_2SiO_4** (Larnite) 9-0951D		**$Ca_2(Al,Fe)_2O_5$** (Brownmillerite) 30-0226*	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
2.9992	100	3.035	178				
2.7915	30			2.795	27	2.784	5.5
2.7025	30			2.731	11		
2.6532	10					2.673	7.7
2.6186	30			2.608	17		
2.5023	40	2.495	25				
2.2904	50	2.285	32	2.304	1.6		
2.1960	20					2.210	1.8
2.1005	40	2.095	32	2.105	1.1		
1.9141	40	1.913	30	1.913	2.7	1.9283	7.7
1.8795	40	1.875	30			1.8813	0.7
1.8194	10			1.821	1.6	1.8149	9.9

TABLE 8. Diffraction lines (d) and relative intensities (I/I_0) of the rest after TG analysis of the sample DDD 36-brown layer compared to lines of the most probable components from µPDSM computer database. For each compound its mineral name and the number of PDF card are given.

The rest after TG DDD 36- brown layer		**CaO** (Lime) 43-1001D		**Ca_2SiO_4** (Larnite) 33-0302*		**$Ca_3Al_2O_6$** 38-1429*		**MgO** (Periclase) 43-1022C		**$Ca_{1.7}Mg_{0.3}SiO_4$** (Bredigite) 35-0260D	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
4.9252	10			4.892	1.4*						
3.3525	10					3.3312	1.3*			3.38	7.1
2.9307	10					2.938	0.7*			2.959	2.8
2.8488	10									2.837	9.2
2.8259	10			2.814	10	2.8342	3.3				
2.7790	50	2.777	63	2.790	46	2.7871	5.4*			2.783	6.3
2.7503	40			2.745	39					2.736	71

TABLE 8 CONTINUE

The rest after TG DDD 36- brown layer		**CaO** (Lime) 43-1001D		**Ca_2SiO_4** (Larnite) 33-0302*		**$Ca_3Al_2O_6$** 38-1429*		**MgO** (Periclase) 43-1022C		**$Ca_{1.7}Mg_{0.3}SiO_4$** (Bredigite) 35-0260D	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
2.6994	40					2.6987	67			2.672	68
2.6384	30										
2.6086	30			2.610	20					2.599	6.3
2.4032	100	2.405	171	2.403	8.6	2.4135	3.3*			2.424	4.9
2.2837	10			2.281	10	2.2752	2.0*				
2.2409	10					2.2506	0.7*			2.233	19
2.2256	10									2.215	14
2.1906	30			2.189	24						
2.1675	10			2.165	6.2					2.176	7.8
2.1030	20			2.103	0.5*			2.106	29	2.113	6.3
2.0815	20			2.083	2.9*					2.081	4.9
2.0534	10			2.050	6.7						
2.0238	10			2.027	7.1					2.028	6.3
1.9955	10									2.004	9.2
1.9876	10			1.987	9.5						
1.9431	20									1.954	4.9
1.9264	20									1.924	20
1.9062	10			1.9115	2.9	1.9079	20			1.899	11
1.7000	80	1.7008	84	1.6964	2.4						
1.6320	10			1.6282	5.7	1.6270	0.7*			1.622	1.4
1.5748	10			1.5738	2.4	1.5744	0.7*			1.576	4.9
1.5554	20					1.5578	16			1.548	4.9
1.4875	10					1.4895	0.7*	1.4895	15		
1.4496	40	1.4504	22								
1.4106	10					1.4110	0.7*				
1.4054	10					1.4050	0.7*				
1.3984	10									1.399	4.9
1.3883	30	1.3887	22			1.3876	0.7*			1.386	1.4

TABLE 8 CONTINUE

The rest after TG DDD 36-brown layer		CaO (Lime) 43-1001D		Ca_2SiO_4 (Larnite) 33-0302*		$Ca_3Al_2O_6$ 38-1429*		MgO (Periclase) 43-1022C		$Ca_{1.7}Mg_{0.3}SiO_4$ (Bredigite) 35-0260D	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
1.3755	10					1.3760	0.7*				
1.3489	10					1.3490	6				
1.2615	20										
1.2158	10					1.2142	0.7*	1.2162	4.4		
1.2022	20	1.2026	9								
1.1518	10										
1.1031	10	1.1036	9								
1.0753	30	1.0757	22								

TABLE 9. Diffraction lines (d) and relative intensities (I/I_0) of the rest after TG analysis of the sample DDD 36-undamaged plaster compared to lines of the most probable components from μPDSM computer database. For each compound its mineral name and the number of PDF card are given.

The rest after TG DDD 36-undamaged plaster		$Ca_2(Al,Fe)_2O_5$ (Brownmillerite) 30-0226*		Cs_2SiO_4 (Larnite) 9-0351D		SiO_2 (Quartz) 5-0490D		Fe_2O_3 (Hematite) 13-0534D		$CaSO_4$ 43-0606I		$Ca_{1.82}Al_{3.64}Si_{0.38}O_8$ 26-0559	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
4.9054	30			4.90	15								
4.2933	20					4.26	31			4.360	4.4		
4.1381	20											4.09	13
4.0073	20												
3.7979	20			3.827	12							3.84	28
3.7529	10			3.783	12								
3.6817	10	3.654	29					3.66	13				
3.4804	40									3.485	70		
3.3637	30	3.406	7	3.377	18								
3.3317	30					3.343	89						
3.2203	10			3.241	21								
3.0267	10			3.046	21								
2.9993	60									3.018	79	2.977	51

TABLE 9 CONTINUE

The rest after TG DDD 36- undamaged plaster		$Ca_2(Al,Fe)_2O_5$ (Brownmillerite) 30-0226*		Cs_2SiO_4 (Larnite) 9-0351D		SiO_2 (Quartz) 5-0490D		Fe_2O_3 (Hematite) 13-0534D		$CaSO_4$ 43-0606I		$Ca_{1.82}Al_{3.64}Si_{0.38}O_8$ 26-0559	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
2.8836	30												
2.8389	40			2.814	30							2.847	4.1
2.7716	90	2.784	46	2.780	136					2.797	44		
2.7378	100			2.744	144					2.723	17		
2.7187	90			2.716	61								
2.7088	10												
2.6835	60	2.673	64					2.69	54				
2.6322	60	2.644	184										
2.5982	80	2.576	31	2.608	98								
2.5314	10			2.543	21								
2.5050	10							2.51	27			2.509	30
2.4447	20			2.451	30	2.458	11						
2.4281	10	2.434	7	2.433	12								
2.3960	80			2.407	30							2.400	3.0
2.3187	40			2.322	9					2.339	8.7	2.307	9.1
2.2787	70			2.282	53	2.282	11	2.285	1.1	2.282	4.4		
2.2353	10					2.237	5.3	2.201	16				
2.1962	10	2.210	15	2.196	18							2.205	2.0
2.1815	40			2.188	98					2.182	8.7	2.173	3.0
2.1607	10	2.155	16	2.163	30								
2.1490	10									2.146	17		
2.1244	10			2.130	18	2.128	8.0					2.138	2.0
2.0985	20			2.094	12					2.104	4.4	2.100	2.0
2.0785	10			2.083	12			2.070	1.1				
2.0446	60	2.051	64	2.048	30							2.042	41
2.0335	10			2.041	18								
2.0195	40			2.019	30					2.013	17		
1.9915	10					1.980	5.3			1.986	4.4		
1.9790	40			1.983	53								

TABLE 9 CONTINUE

The rest after TG DDD 36-undamaged plaster		$Ca_2(Al,Fe)_2O_5$ (Brownmillerite) 30-0226*		Cs_2SiO_4 (Larnite) 9-0351D		SiO_2 (Quartz) 5-0490D		Fe_2O_3 (Hematite) 13-0534D		$CaSO_4$ 43-0606I		$Ca_{1.82}Al_{3.64}Si_{0.38}O_8$ 26-0559	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
1.9424	30												
1.9320	30	1.9283	64										
1.9161	40			1.913	15					1.917	17	1.919	13
1.9042	50			1.897	9								
1.8653	10	1.8632	16										
1.8367	20			1.845	9			1.838	22	1.848	35	1.846	2.0
1.8126	10	1.8149	82	1.821	9	1.817	15						
1.7995	40			1.808	18	1.801	0.9						
1.7882	20	1.7952	5	1.791	18								
1.7661	10			1.768	9								
1.7504	40									1.743	26		
1.7359	10	1.7327	13	1.727	9								
1.7266	10			1.718	9								
1.6977	30			1.707	21					1.697	26	1.699	5.1
1.6861	40							1.690	32	1.680	8.7		
1.6327	30			1.634	21			1.634	2.2				
1.6279	30			1.627	12					1.618	4.4		
1.6007	10			1.603	9	1.608	0.9	1.596	8.6				
1.5841	10	1.5784	26	1.587	9							1.584	2.0
1.5713	20	1.5638	7	1.575									
1.5528	30			1.552	15								
1.5378	20	1.5380	26			1.541	13			1.546	4.4		
1.5255	10	1.5202	13	1.523	12					1.526	4.4	1.529	7.1
1.5116	10												
1.4999	10	1.5013	15							1.509	26		
1.4915	50												
1.4824	40			1.485	12			1.484	19	1.479	8.7		
1.4699	20												

TABLE 9 CONTINUE

The rest after TG DDD 36-undamaged plaster		$Ca_2(Al,Fe)_2O_5$ (Brownmillerite) 30-0226*		Cs_2SiO_4 (Larnite) 9-0351D		SiO_2 (Quartz) 5-0490D		Fe_2O_3 (Hematite) 13-0534D		$CaSO_4$ 43-0606I		$Ca_{1.82}Al_{3.64}Si_{0.38}O_8$ 26-0559	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
1.4476	10	1.4524	7	1.445	12	1.453	2.7	1.452	19			1.449	13
1.4361	10									1.437	4.4		
1.3744	10					1.375	9.7						
1.3708	10	1.3669	5			1.372	8.0						
1.3661	10	1.3588	9									1.369	2.0
1.2561	10					1.256	3.5	1.258	4.3				
1.2518	20												
1.1788	10					1.1802	3.5						
1.1384	10					1.1408	0.9*	1.141	6.5	1.141	26		

TABLE 10. Diffraction lines (d) and relative intensities (I/I_0) of the sample ZAP 10-brown layer compared to lines of the most probable components from μPDSM computer database. For each compound its mineral name and the number of PDF card are given.

SAMPLE ZAP 10-brown layer		$CaSO_4{\cdot}2H_2O$ (Gypsum) 21-0816*		$CaCO_3$ (Calcite) 24-0027D		$Mg_3Ca(CO_3)_4$ (Huntite) 14-409I	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
7.6179	90	7.61	108				
4.2806	100	4.28	216				
3.8506	10			3.852	43		
3.7996	20	3.80	19				
3.0668	80	3.07	72				
3.0312	80			3.030	148		
2.8747	70	2.871	240			2.888	44
2.8230	40			2.834	3*	2.833	222
2.7845	30	2.788	48				
2.7276	10					2.744	4
2.6808	70	2.684	120				

TABLE 10 CONTINUE

SAMPLE ZAP 10- brown layer		**$CaSO_4 \cdot 2H_2O$** (Gypsum) 21-0816*		**$CaCO_3$** (Calcite) 24-0027D		**$Mg_3Ca(CO_3)_4$** (Huntite) 14-409I	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
2.6394	10						
2.5913	10	2.595	5			2.604	27
2.5360	10						
2.4934	50	2.496	48	2.495	10*		
2.4529	20	2.454	14			2.432	22
2.2817	50			2.284	27	2.284	13
2.2169	50	2.220	14				
2.0882	60	2.087	34	2.094	40		
2.0734	50	2.073	48				
1.9946	30	1.993	5			1.991	22
1.9265	10			1.9261	6		
1.9101	20			1.9071	25		
1.8990	20	1.900	10			1.896	13
1.8757	40	1.880	14	1.8726	50		
1.8126	20	1.812	10			1.821	4
1.7982	20	1.798	14			1.796	4
1.7616	20					1.765	44
1.6662	10	1.664	10			1.656	2*
1.6444	10	1.646	5				
1.6212	30	1.622	10	1.6259	3*	1.611	2*
1.4391	20	1.440	10	1.4405	7	1.445	4
1.4196	10	1.418	5	1.4168	4	1.418	4
1.2616	10						
1.1526	10			1.1536	4		

TABLE 11. Diffraction lines (d) and relative intensities (I/I_0) of the sample ZAP 10-undamaged plaster compared to lines of the most probable components from μPDSM computer database. For each compound its mineral name and the number of PDF card are given.

SAMPLE ZAP 10-undamaged plaster		**$CaCO_3$** (Calcite) 5-0586*		**$CaSO_4 \cdot 2H_2O$** (Gypsum) 36-0432D	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
7.6179	30			7.59	112
4.2806	30			4.279	146
3.8506	40	3.86	39	3.795	19
3.3463	30				
3.0668	10			3.061	80
3.0312	100	3.035	321		
2.8855	30			2.875	61
2.7845	10			2.789	12
2.6812	10			2.683	45
2.4914	50	2.495	45	2.499	12
2.2817	50	2.285	58		
2.2143	10			2.215	13
2.1924	20				
2.0917	60	2.095	58	2.087	16
1.9250	30	1.927	16		
1.9094	60	1.913	55	1.8973	13
1.8731	60	1.875	55	1.8781	12
1.6244	30	1.626	13	1.6199	7
1.6031	40	1.604	26		
1.5239	40	1.525	16		
1.4391	40	1.440	16	1.4396	3*
1.4272	10	1.422	10		
1.4206	30				
1.1526	30	1.1538	10		

TABLE 12. Diffraction lines (d) and relative intensities (I/I_0) of the rest after TG analysis of the sample ZAP 10-brown layer compared to lines of the most probable components from µPDSM computer database. For each compound its mineral name and the number of PDF card are given.

The rest after TG ZAP 10-brown layer		$CaSO_4$ (Anhydrite) 6-0226D		CaO (Lime) 37-1497*		SiO_2 (Quartz) 33-1161*		$CaAl_{12}O_9$ 25-0122D		CuO 44-0706O		$Ca_5MgSi_3O_{12}$ 34-1350O	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
4.9167	10												
4.2650	20					4.257	24						
4.0263	10							4.019	2.2*				
3.8780	40	3.87	28									3.891	1.8
3.7773	10												
3.4860	100	3.498	471									3.489	5.9
3.3495	30					3.342	108					3.377	7.1
3.2799	10											3.320	7.7
3.2172	10											3.227	3.5
3.1218	30	3.118	19										
3.0040	10												
2.8997	10							2.907	4.4			2.906	5.3
2.8493	90	2.849	165									2.871	2.4
2.8251	10											2.837	11
2.7973	30	2.797	19										
2.7741	50			2.7774	54			2.781	24	2.7752	7.6	2.758	3.5
2.7252	10							2.735	6.6			2.727	47
2.6980	20							2.695	1.3*	2.7047	6.0*	2.687	24
2.6367	20											2.655	15
2.6180	10							2.622	44			2.602	3.0
2.5822	10											2.581	5.9
2.5449	10									2.5444	28	2.558	4.7
2.5145	10											2.525	3.5
2.4710	50	2.473	38					2.479	44			2.454	1.8
2.4294	10											2.426	5.9
2.4040	80			2.4059	149			2.408	2.2			2.391	7.7
2.3468	10							2.352	8.7	2.3380	32	2.345	3.5

TABLE 12 CONTINUE

The rest after TG ZAP 10- brown layer		$CaSO_4$ (Anhydrite) 6-0226D		CaO (Lime) 37-1497*		SiO_2 (Quartz) 33-1161*		$CaAl_{12}O_9$ 25-0122D		CuO 44-0706O		$Ca_5MgSi_3O_{12}$ 34-1350O	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
2.3270	90	2.328	94									2.322	8.3
2.2841	10					2.282	9	2.287	13				
2.2646	10											2.269	18
2.2379	10					2.237	4					2.236	21
2.2087	90	2.208	94					2.211	4.4*			2.216	0.6
2.1814	60	2.183	38					2.188	4.4*				
2.1654	30											2.169	9.5
2.1129	10							2.110	26			2.112	4.1
2.0844	70	2.086	47									2.086	9.5
2.0472	10									2.0474	6.4	2.062	7.7
2.0162	10							2.010	15			2.008	12
1.9938	60	1.993	28										
1.9375	40	1.938	19									1.928	24
1.9230	10											1.914	11
1.9034	10							1.908	1.3*			1.903	12
1.8845	10												
1.8687	90	1.869	75							1.8722	13*		
1.8523	40	1.852	19										
1.8411	10							1.838	2.2*			1.841	11
1.8305	10												
1.8223	10					1.8179	15						
1.7986	10					1.8021	1*						
1.7798	10									1.7814	6.0		
1.7702	20												
1.7491	90	1.749	56										
1.7346	10												
1.7157	10							1.720	1.3	1.7168	8.3		
1.7004	70			1.7009	80								

TABLE 12 CONTINUE

The rest after TG ZAP 10- brown layer		**$CaSO_4$** (Anhydrite) 6-0226D		**CaO** (Lime) 37-1497*		**SiO_2** (Quartz) 33-1161*		**$CaAl_{12}O_9$** 25-0122D		**CuO** 44-0706O		**$Ca_5MgSi_3O_{12}$** 34-1350O	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
1.6763	10					1.6719	4	1.681	1.3*				
1.6482	80	1.648	66										
1.6091	10					1.6082	1*	1.605	4.4				
1.5941	30	1.594	19										
1.5649	30	1.564	28					1.563	2.2*				
1.5419	20					1.5418	10	1.540	6.6				
1.5363	10							1.534	28				
1.5251	50	1.525	19*					1.525	1.3*				
1.5147	10	1.515	9					1.515	8.7	1.5102	11		
1.4904	50	1.490	28					1.487	1.3*				
1.4508	40			1.4505	24	1.4536	1*	1.454	2.2*				
1.4432	10												
1.4386	10												
1.4249	40	1.424	19										
1.4187	20	1.418	9			1.4189	1*			1.4164	10		
1.4119	10												
1.3973	40	1.398	19										
1.3886	40			1.3888	24			1.388	31				
1.3773	10					1.3752	8	1.380	4.4	1.3801	11		
1.3714	10					1.3718	9						
1.3651	10	1.365	9										
1.3482	10							1.347	1.3*				
1.3200	60	1.319	19*										
1.2977	10	1.296	9										
1.2769	60	1.277	28										
1.2298	10					1.2285	1*						
1.2227	10												
1.2188	10												

TABLE 12 CONTINUE

The rest after TG ZAP 10-brown layer		$CaSO_4$ (Anhydrite) 6-0226D		CaO (Lime) 37-1497*		SiO_2 (Quartz) 33-1161*		$CaAl_{12}O_9$ 25-0122D		CuO 44-0706O		$Ca_5MgSi_3O_{12}$ 34-1350O	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
1.2165	30	1.216	19										
1.2082	10												
1.2022	30			1.2026	9*								
1.1992	10	1.1993	9			1.1999	2			1.1968	7.3		
1.1904	10												
1.1843	10					1.1843	3						
1.1731	10												
1.1656	40	1.1663	19										
1.1603	10									1.1586	7.6		
1.1519	10					1.1532	1*						
1.1491	20	1.1483	9										
1.1434	10												
1.1417	10					1.1405	1*						
1.1071	40	1.1062	28										
1.1041	40	1.1044	19	1.1037	9*								
1.0956	10												
1.0927	10									1.0922	8.0		
1.0888	10												
1.0838	10												
1.0789	30	1.0785	9*										
1.0760	40			1.0758	24					1.0742	7.3		
1.0431	30					1.0438	1*						
1.0405	30												
1.0313	10												

TABLE 13. Diffraction lines (d) and relative intensities (I/I_0) of the rest after TG analysis of the sample ZAP 10-undamaged plaster compared to lines of the most probable components from µPDSM computer database. For each compound its mineral name and the number of PDF card are given.

The rest after TG ZAP 10-undamaged plaster		$CaSO_4$ (Anhydrite) 6-0226D		CaO (Lime) 37-1497*		SiO_2 (Quartz) 5-0490D		$Ca_5MgSi_3O_{12}$ 34-1350O		$Ca(OH)_2$ (Portlandite) 4-0733D		$Ca_{54}MgAl_2Si_{16}O_{90}$ 13-0272	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
4.9167	10									4.9	50		
4.2691	10					4.26	13						
3.4995	50	3.498	82					3.500	2.2*				
3.3489	30					3.343	38						
3.2699	10												
3.1207	30	3.118	3.3*							3.112	15		
3.0947	30												
3.0325	10											3.034	11
3.0095	10												
2.9766	10											2.973	4.6
2.8497	30	2.849	29					2.837	4.2*				
2.8097	20	2.797	3.3*										
2.7762	70			2.7774	52							2.776	23
2.7435	20							2.742	18			2.748	9.2
2.7123	10							2.727	18				
2.6949	10							2.687	8.9				
2.6722	20							2.674	22				
2.6386	60									2.628	67		
2.6165	60											2.608	16
2.4736	10	2.473	6.5										
2.4033	100			2.4059	144								
2.3296	20	2.328	16					2.322	3.1*			2.323	2.3
2.2956	10							2.302	0.4*				
2.2668	10							2.269	6.7				
2.2397	10					2.237	2.3	2.236	7.8				
2.2079	20	2.208	16					2.216	0.2				
2.1880	40	2.183	6.5									2.184	9.2

TABLE 13 CONTINUE

The rest after TG ZAP 10- undamaged plaster		$CaSO_4$ (Anhydrite) 6-0226D		CaO (Lime) 37-1497*		SiO_2 (Quartz) 5-0490D		$Ca_5MgSi_3O_{12}$ 34-1350O		$Ca(OH)_2$ (Portlandite) 4-0733D		$Ca_{54}MgAl_2Si_{16}O_{90}$ 13-0272	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
2.0487	10												
1.9471	40												
1.9381	40	1.938	3.3*									1.938	2.3
1.9199	40							1.914	4.2*	1.927	28		
1.8879	10												
1.8703	20	1.869	13										
1.8016	50					1.801	0.4*						
1.7928	50									1.796	24		
1.7488	10	1.749	9.8										
1.7282	10												
1.7003	80			1.7009	78								
1.6861	10									1.687	14		
1.6461	10	1.648	11										
1.5364	10					1.541	5.7					1.541	2.3
1.4906	20	1.490	4.9*									1.490	4.6
1.4508	30			1.4505	23	1.453	1.1			1.449	8.7		
1.3882	20			1.3888	23								
1.3740	10					1.375	4.2						
1.2766	10	1.277	4.9										
1.1068	10	1.1062	4.9										
1.0768	30	1.0785	1.6*										
1.0755	30			1.0758	23								

TABLE 14. Diffraction lines (d) and relative intensities (I/I_0) of the sample AUE 37-brown layer compared to lines of the most probable components from µPDSM computer database. For each compound its mineral name and the number of PDF card are given.

SAMPLE AUE 37-brown layer		**$CaSO_4 \cdot 2H_2O$** (Gypsum) 33-0311*		**Ca_2SiO_4** (Larnite) 9-0351D		**SiO_2** (Quartz) 5-0490D		**$CaCO_3$** (Calcite) 5-0586*		**$Ca_3Mg(SiO_4)_2$** (Merwinite) 35-0591*	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
7.6034	10	7.63	54								
4.2941	50	4.283	54			4.26	38			4.3350	1.4
3.3457	90					3.343	110				
3.2942	10									3.3248	1.4
3.1977	10									3.1689	3.2
3.0650	40	3.065	41							3.0666	0.9
3.0506	100			3.046	6.8*			3.035	89		
2.8798	50	2.873	24	2.876	17						
2.7998	30	2.789	5.4*	2.795	49					2.8164	0.9
2.7761	30			2.780	44						
2.7402	20	2.732	1.1*	2.744	46					2.7562	12
2.6965	70									2.6865	46
2.6750	10	2.685	19							2.6712	30
2.6375	20									2.6530	21
2.6019	10	2.597	3.3	2.608	32						
2.4921	10	2.495	6.0					2.495	12	2.5086	0.5
2.4569	20	2.452	3.3*	2.451	9.7	2.458	13			2.4648	1.4
2.4246	20			2.433	3.9*						
2.4009	20	2.406	2.2*	2.400	9.7						
2.3761	10										
2.3144	10			2.304	2.9					2.3206	5.5
2.2801	30			2.282	17	2.282	13	2.285	16	2.2851	3.2
2.1927	10			2.196	5.8					2.1916	0.9
2.0911	10	2.086	14	2.094	3.9			2.095	16	2.1000	0.5
1.9231	10							1.927	4.4		
1.9077	10			1.913	4.9			1.913	15	1.9111	16
1.8728	10	1.8795	6.5					1.875	15	1.8787	11

TABLE 14 CONTINUE

SAMPLE AUE 37- brown layer		**$CaSO_4 \cdot 2H_2O$** (Gypsum) 33-0311*		**Ca_2SiO_4** (Larnite) 9-0351D		**SiO_2** (Quartz) 5-0490D		**$CaCO_3$** (Calcite) 5-0586*		**$Ca_3Mg(SiO_4)_2$** (Merwinite) 35-0591*	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
1.8212	20			1.821	2.9*	2.817	19			1.8258	0.5
1.7857	10	1.7844	4.9	1.791	5.8						
1.3715	10					1.375	12				
1.3449	10	1.3440	0.5*								

TABLE 15. Diffraction lines (d) and relative intensities (I/I_0) of the sample AUE 37-undamaged plaster compared to lines of the most probable components from µPDSM computer database. For each compound its mineral name and the number of PDF card are given.

SAMPLE AUE 37- undamaged plaster		**$CaSO_4 \cdot 2H_2O$** (Gypsum) 33-0311*		**Ca_2SiO_4** (Larnite) 33-0302*		**SiO_2** (Quartz) 5-0490D		**$CaCO_3$** (Calcite) 24-0027D		**$Ca_{14}Mg_2(SiO_4)_8$** (Bredigite) 36-0399*		**$Ca_2Al_{1.38}Fe_{0.62}O_5$** 42-1469*	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
7.6002	10	7.63	140										
7.2767	20											7.2485	22
4.2495	40	4.283	140			4.26	70			4.19	4*		
3.8499	10			3.824	8			3.852	43	3.849	9	3.8258	2
3.7594	10	3.799	24	3.786	8					3.797	6		
3.5893	10									3.586	2*	3.6332	20
3.5374	10									3.566	4		
3.4737	40									3.485	13		
3.4091	20			3.378	11					3.372	19		
3.3377	80					3.343	200					3.3819	9
3.2369	10			3.241	9								
3.1798	10	3.172	6	3.176	8								
3.1056	10												
3.0670	10	3.065	105	3.049	14								

TABLE 15 CONTINUE

SAMPLE AUE 37- undamaged plaster		**$CaSO_4{\cdot}2H_2O$** (Gypsum) 33-0311*		**Ca_2SiO_4** (Larnite) 33-0302*		**SiO_2** (Quartz) 5-0490D		**$CaCO_3$** (Calcite) 24-0027D		**$Ca_{14}Mg_2(SiO_4)_8$** (Bredigite) 36-0399*		**$Ca_2Al_{1.38}Fe_{0.62}O_5$** 42-1469*	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
3.0299	100							3.030	148				
2.9704	20									2.955	11		
2.8821	60	2.873	63	2.877	33								
2.8131	30			2.814	35					2.835	30		
2.7791	70	2.789	14	2.783	158					2.778	11*		
2.7508	60			2.745	131					2.737	142	2.7567	33
2.7280	30	2.732	3*	2.718	47					2.723	152		
2.6910	70	2.685	49										
2.6676	30									2.669	190	2.6535	55
2.6353	60									2.638	8*	2.6293	109
2.6048	60			2.610	66					2.598	13		
2.5751	10	2.597	8							2.584	8*	2.5643	14
2.5493	30	2.534	3*	2.545	14					2.553	9		
2.4888	20	2.495	15					2.495	10*	2.484	8		
2.4559	20	2.452	8	2.448	19	2.458	24			2.448	13		
2.4058	20	2.406	6	2.410	20					2.423	13	2.4130	3
2.3813	20			2.403	28								
2.3581	20									2.344	15		
2.3288	30			2.323	3*								
2.3039	10	2.291	1*	2.301	6								
2.2812	80			2.281	35	2.282	24	2.284	27				
2.2560	20												
2.2359	20					2.237	12			2.232	47		
2.2125	30	2.219	21							2.213	38	2.1938	13
2.1884	60			2.189	80								
2.1661	30			2.165	20					2.176	23		
2.1469	20											2.1406	16
2.1260	10	2.142	3	2.129	11	2.128	18			2.111	13		

TABLE 15 CONTINUE

SAMPLE AUE 37- undamaged plaster		**$CaSO_4 \cdot 2H_2O$** (Gypsum) 33-0311*		**Ca_2SiO_4** (Larnite) 33-0302*		**SiO_2** (Quartz) 5-0490D		**$CaCO_3$** (Calcite) 24-0027D		**$Ca_{14}Mg_2(SiO_4)_8$** (Bredigite) 36-0399*		**$Ca_2Al_{1.38}Fe_{0.62}O_5$** 42-1469*	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
2.1061	10			2.103	2					2.106	9		
2.0936	30	2.086	35	2.091	9			2.094	40				
2.0844	40									2.083	13		
2.0756	20	2.074	21	2.083	9					2.073	27		
2.0486	30	2.048	8	2.050	22							2.0412	27
2.0290	30	2.032	1*	2.027	24					2.029	9		
2.0187	30			2.020	24					2.024	11		
1.9836	20	1.992	6	1.982	38	1.980	12						
1.9234	10			1.9115	9			1.9261	6	1.924	57		
1.9054	30	1.8998	22	1.8979	14			1.9071	25	1.902	23	1.9118	38
1.8724	20	1.8795	20					1.8726	50			1.8696	3*
1.8550	10	1.8650	4									1.8487	12
1.8370	10			1.8441	6					1.838	19		
1.8166	40	1.8118	18	1.8210	5	1.817	34					1.8111	16
1.8030	20	1.7995	8	1.8018	14	1.801	2						
1.7851	20	1.7844	13	1.7899	11							1.7853	2
1.7642	20			1.7657	2*								
1.7275	10			1.7270	8							1.7173	7
1.6694	30					1.672	14			1.670	8		
1.6643	20	1.6640	8							1.663	8		
1.6555	10					1.659	6			1.660	4*		
1.6423	10	1.6456	6							1.649	6		
1.6379	10									1.639	2		
1.6236	20	1.6209	13	1.6282	19			1.6259	3*	1.622	8		
1.6050	20			1.6110	16	1.608	2	1.6040	22	1.613	4*		
1.6008	20	1.6005	1*	1.6040	17					1.604	4		
1.5847	10	1.5846	6	1.5874	9					1.583	6		
1.5718	20			1.5738	8					1.576	13	1.5798	2

TABLE 15 CONTINUE

SAMPLE AUE 37-undamaged plaster		$CaSO_4 \cdot 2H_2O$ (Gypsum) 33-0311*		Ca_2SiO_4 (Larnite) 33-0302*		SiO_2 (Quartz) 5-0490D		$CaCO_3$ (Calcite) 24-0027D		$Ca_{14}Mg_2(SiO_4)_8$ (Bredigite) 36-0399*		$Ca_2Al_{1.38}Fe_{0.62}O_5$ 42-1469*	
d [Å]	I/I$_0$	d [Å]	I/I$_0$	d [Å]	I/I$_0$	d [Å]	I/I$_0$	d [Å]	I/I$_0$	d [Å]	I/I$_0$	d [Å]	I/I$_0$
1.5579	10									1.559	27	1.5649	16
1.5532	30									1.553	13		
1.5414	30					1.541	30			1.548	11		
1.5322	10	1.5327	3									1.5278	16
1.4910	20	1.4947	1*									1.4955	8
1.4840	10												
1.4614	10	1.4591	4										
1.4511	20					1.453	6					1.4485	4
1.4401	20	1.4392	7					1.4405	7				
1.4031	10	1.4015	3									1.4095	4
1.3874	10											1.3891	5
1.3808	20					1.382	14						
1.3744	40					1.375	22						
1.3662	20	1.3657	7			1.372	18						
1.3566	10											1.3546	3
1.3475	10	1.3440	1*										

TABLE 16. Diffraction lines (d) and relative intensities (I/I_0) of the rest after TG analysis of the sample AUE 37-brown layer compared to lines of the most probable components from µPDSM computer database. For each compound its mineral name and the number of PDF card are given.

The rest after TG AUE 37-brown layer		SiO_2 (Quartz) 5-0490D		$CaSO_4$ (Anhydrite) 6-0226D		Ca_2SiO_4 (Larnite) 9-0351D		CaO-MgO-Al_2O_3-SiO_2 17-0736O		$Ca(Mg,Al)(Si,Al)_2O_6$ (Diopside) 41-1370*		$KAlSi_3O_8$ (Microcline) 22-0675D	
d [Å]	I/I$_0$	d [Å]	I/I$_0$	d [Å]	I/I$_0$	d [Å]	I/I$_0$	d [Å]	I/I$_0$	d [Å]	I/I$_0$	d [Å]	I/I$_0$
7.2648	10												
4.3949	10									4.434	5.7		
4.2849	10	4.26	33									4.285	50

TABLE 16 CONTINUE

The rest after TG AUE 37- brown layer		SiO_2 (Quartz) 5-0490D		$CaSO_4$ (Anhydrite) 6-0226D		Ca_2SiO_4 (Larnite) 9-0351D		CaO-MgO-Al_2O_3-SiO_2 17-0736O		$Ca(Mg,Al)(Si,Al)_2O_6$ (Diopside) 41-1370*		$KalSi_3O_8$ (Microcline) 22-0675D	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
3.8772	30			3.87	26							3.856	6.1
3.8360	10					3.827	5.2						
3.7649	20					3.783	5.2*	3.76	9.8			3.746	32
3.7322	20							3.72	20				
3.5709	20											3.593	7.1
3.5555	20											3.563	7.8
3.4965	100			3.498	438							3.515	6.1
3.4388	20											3.474	40
3.3469	50	3.343	95							3.339	5.7*	3.335	46
3.2894	10							3.27	2.4*			3.292	87
3.2294	20					3.241	9.1			3.220	47	3.241	83
3.1820	10					3.175	7.8						
3.1221	10			3.118	18								
3.0670	20							3.09	39				
3.0249	20							3.01	9.8			3.005	23
2.9937	30									2.958	95	2.979	25
2.9651	20							2.97	2.4			2.946	4.3
2.9286	20							2.94	9.8	2.943	52		
2.8907	20							2.88	49	2.891	28	2.898	23
2.8771	20					2.876	23						
2.8485	80			2.849	153								
2.8240	20					2.814	13	2.81	20				
2.7917	40			2.797	18	2.795	65						
2.7674	40					2.780	59	2.776	49			2.774	9.6
2.7496	50					2.744	62						
2.7191	20					2.731	26	2.715	20				
2.6945	40												
2.6665	30							2.656	2.4				

TABLE 16 CONTINUE

The rest after TG AUE 37- brown layer		SiO_2 (Quartz) 5-0490D		$CaSO_4$ (Anhydrite) 6-0226D		Ca_2SiO_4 (Larnite) 9-0351D		$CaO-MgO-Al_2O_3-SiO_2$ 17-0736O		$Ca(Mg,Al)(Si,Al)_2O_6$ (Diopside) 41-1370*		$KalSi_3O_8$ (Microcline) 22-0675D	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
2.6765	40												
2.6048	20					2.608	42					2.612	7.8
2.5444	20					2.543	9.1	2.550	2.4	2.555	19	2.556	18
2.5198	20							2.521	9.8	2.512	28	2.528	4.3
2.4712	40			2.473	35			2.463	9.8				
2.4562	20	2.458	11			2.451	13	2.452	9.8			2.463	0.9
2.4405	20					2.433	5.2*	2.434	9.8			2.420	4.3
2.4052	20					2.407	13	2.409	9.8			2.401	6.1
2.3752	20												
2.3525	10							2.362	20			2.366	3.5
2.3271	80			2.328	88	2.322	3.9*	2.336	9.8			2.329	5.2
2.3022	20					2.304	3.9			2.301	13		
2.2854	10	2.282	11			2.282	23					2.278	1.7
2.2394	10	2.237	5.7					2.245	20	2.228	3.8	2.251	1.7
2.2050	90			2.208	88	2.196	7.8			2.204	5.7	2.207	1.7
2.1813	50			2.183	35	2.188	42					2.192	2.6
2.1474	30									2.146	15	2.160	14
2.1148	10									2.125	17	2.115	7.8
2.1033	30							2.107	20	2.102	11		
2.0851	70			2.086	44	2.083	5.2*						
2.0657	10							2.067	9.8			2.065	2.6
2.0483	30					2.048	13					2.049	3.5
2.0365	30							2.038	39	2.032	11		
2.0251	20					2.026	13	2.027	20				
2.0151	10					2.019	13			2.018	6.6	2.017	3.5
1.9920	40			1.993	26							2.000	4.3
1.9760	10	1.980	5.7			1.983	23	1.975	9.8	1.969	5.7	1.980	4.3
1.9383	40			1.938	18			1.936	39			1.947	1.7

TABLE 16 CONTINUE

The rest after TG AUE 37-brown layer		SiO_2 (Quartz) 5-0490D		$CaSO_4$ (Anhydrite) 6-0226D		Ca_2SiO_4 (Larnite) 9-0351D		CaO-MgO-Al_2O_3-SiO_2 17-0736O		$Ca(Mg,Al)(Si,Al)_2O_6$ (Diopside) 41-1370*		$KAlSi_3O_8$ (Microcline) 22-0675D	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
1.9238	30											1.928	6.1
1.9041	30					1.897	3.9						
1.8831	30												
1.8666	80			1.869	70								
1.8515	30			1.852	18	1.845	3.9					1.859	3.5
1.8328	20									1.832	8.5		
1.8151	50	1.817	16*			1.821	3.9*						
1.7468	80			1.749	53					1.742	8.5		
1.6468	80			1.648	61								
1.6012	10					1.604	3.9			1.610	4.7		
1.5926	20			1.594	18					1.592	1.9		
1.5736	20					1.575	7.8			1.581	1.9		
1.5624	30			1.564	26					1.560	2.8		
1.5532	40					1.552	6.5*						
1.5448	10	1.541	14							1.5418	3.8		
1.5361	20									1.5291	2.8*		
1.5241	40			1.525	18	1.523	5.2*			1.5236	4.7		
1.4889	70			1.490	26*	1.485	5.2*			1.4911	0.9*		
1.4243	40			1.424	18					1.4192	9.5		
1.3963	30			1.398	18	1.397	3.9*			1.4006	1.9		
1.3738	30	1.375	10							1.3741	1.9*		
1.3464	20												
1.3188	20			1.319	18					1.3256	3.8		
1.3035	10												
1.2958	20			1.296	9								
1.2761	50			1.277	26								
1.2150	40			1.216	18					1.2182	0.9		
1.2035	10									1.2055	0.9		

TABLE 16 CONTINUE

The rest after TG AUE 37-brown layer		SiO_2 (Quartz) 5-0490D		$CaSO_4$ (Anhydrite) 6-0226D		Ca_2SiO_4 (Larnite) 9-0351D		$CaO-MgO-Al_2O_3-SiO_2$ 17-0736O		$Ca(Mg,Al)(Si,Al)_2O_6$ (Diopside) 41-1370*		$KalSi_3O_8$ (Microcline) 22-0675D	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
1.2012	10	1.1997	4.7	1.1993	9								
1.1781	10	1.1802	3.8	1.1781	4								
1.1655	40			1.1663	18								
1.1482	20			1.1483	9								
1.1052	40			1.1062	26								
1.0779	20			1.0785	9								

TABLE 17. Diffraction lines (d) and relative intensities (I/I_0) of the rest after TG analysis of the sample AUE 37-undamaged plaster compared to lines of the most probable components from µPDSM computer database. For each compound its mineral name and the number of PDF card are given.

The rest after TG AUE 37-undamaged plaster		SiO_2 (Quartz) 5-0490D		$Ca_2Al(Al,Si)_2O_7$ (Gehlenite) 25-0123D		Al_2O_3 (Corundum) 42-1468*		$Ca_{54}MgAl_2Si_{16}O_{90}$ 13-0272		$CaAl_2SiO_6$ 31-0249I		Ca_2SiO_4 (Larnite) 24-0037D	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
7.2648	10												
4.2605	40	4.26	70	4.24	8.0*					4.33	4.9	4.264	6
3.8303	30											3.827	2*
3.7664	20			3.72	27								
3.5639	20												
3.4945	50			3.45	1.8*	3.48	41						
3.3475	100	3.343	201									3.378	6
3.0841	30			3.07	22								
3.0329	40							3.039	39			3.048	15
2.9747	40							2.973	15	2.94	81		
2.8812	30			2.857	88					2.904	28	2.878	30
2.7841	90							2.776	77			2.793	112
2.7516	90			2.730	13*			2.748	31			2.748	124
2.6961	90											2.717	123

TABLE 17 CONTINUE

The rest after TG AUE 37- undamaged plaster		SiO_2 (Quartz) 5-0490D		$Ca_2Al(Al,Si)_2O_7$ (Gehlenite) 25-0123D		Al_2O_3 (Corundum) 42-1468*		$Ca_{54}MgAl_2Si_{16}O_{90}$ 13-0272		$CaAl_2SiO_6$ 31-0249I		Ca_2SiO_4 (Larnite) 24-0037D	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
2.6375	80											2.610	97
2.6085	80							2.608	54			2.582	24
2.5486	50					2.551	56			2.535	33	2.546	7*
2.5185	20			2.535	13					2.509	24	2.503	16
2.4881	10									2.478	41	2.493	33
2.4498	20	2.458	24	2.441	27							2.452	4
2.4061	60			2.406	27								
2.3782	40					2.379	24						
2.3434	30									2.340	3.3*		
2.3302	30							2.323	7.7				
2.2943	20			2.299	18							2.305	22
2.2820	50	2.282	24							2.274	16	2.282	46
2.2487	10	2.237	12										
2.1892	80			2.199	2.7*			2.184	31	2.188	13*	2.189	79
2.1276	30	2.128	18									2.132	4
2.1040	40									2.106	16	2.106	24
2.0844	50					2.085	58			2.090	16	2.084	20
2.0672	10									2.075	9.8	2.065	5
2.0501	30			2.048	8.8							2.047	26
2.0221	30											2.026	7
2.0146	20									2.005	15	2.021	5
1.9834	30	1.980	12					1.983	7.7	1.991	28	1.984	29
1.9411	30							1.938	7.7	1.948	9.8*		
1.9238	20			1.930	49								
1.9048	20											1.894	36
1.8688	10			1.872	7.1								
1.8494	10			1.860	3.5							1.847	7
1.8210	20	1.817	34	1.819	49			1.823	7.7	1.808	4.9	1.821	6

TABLE 17 CONTINUE

The rest after TG AUE 37- undamaged plaster		SiO_2 (Quartz) 5-0490D		$Ca_2Al(Al,Si)_2O_7$ (Gehlenite) 25-0123D		Al_2O_3 (Corundum) 42-1468*		$Ca_{54}MgAl_2Si_{16}O_{90}$ 13-0272		$CaAl_2SiO_6$ 31-0249I		Ca_2SiO_4 (Larnite) 24-0037D	
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	I/I_0
1.7636	20			1.7608	40			1.766	31			1.762	9
1.6979	10									1.703	13	1.697	12
1.6495	10	1.659	6									1.659	5
1.6003	20	1.608	2*			1.6014	48			1.596	16	1.597	4
1.5529	30												
1.5414	20	1.541	30			1.5459	1.2*	1.541	7.7	1.540	3.3		
1.5225	20												
1.5094	20					1.5109	4.1*			1.512	24		
1.4882	40							1.488	15	1.497	16		
1.4041	30					1.4045	17			1.399	15		
1.3825	30	1.382	14	1.3790	22					1.382	24		
1.3747	30	1.375	22			1.3738	26						
1.1997	20	1.1997	10							1.202	1.6		

FIGURE 3. The Mössbauer spectrum of ^{57}Fe in sample DDD 36-undamaged plaster underneath the brown layer at room temperature I – $Fe^{3+}_{(1)}$ - tetrahedral sites, II – $Fe^{3+}_{(2)}$ - octahedral sites

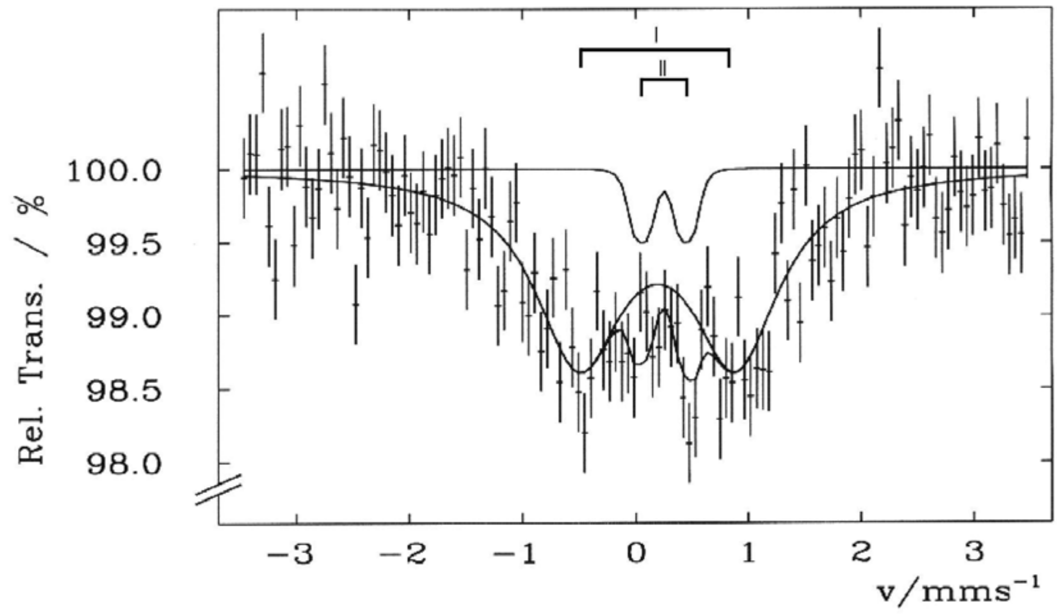


FIGURE 4. The Mössbauer spectrum of ^{57}Fe in sample DDD 36-brown layer at room temperature I – $Fe^{3+}_{(1)}$ - tetrahedral sites, III – $Fe^{3+}_{(3)}$ - octahedral sites

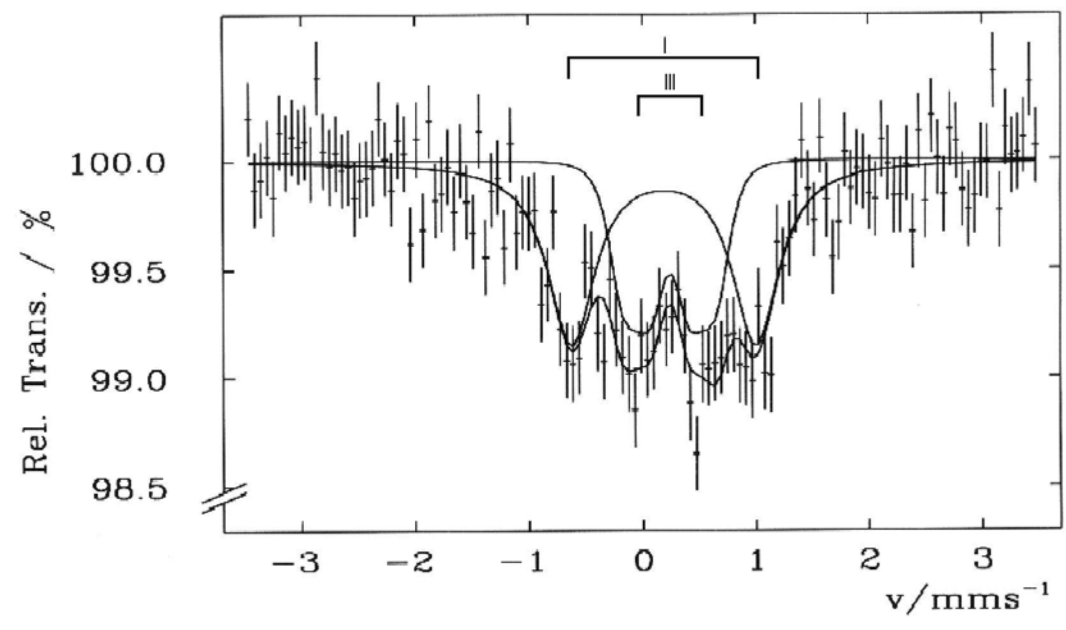


TABLE 18. Hyperfine parameters of Mössbauer spectrum of the sample DDD 36 at room temperature
a.) undamaged plaster
b.) brown layer

	oxidation state	surface area	isomer shift δ [mm/s]	quadrupole splitting ΔE_Q[mm/s]	line width Γ [mm/s]	relative intensity [%]
a.)	$Fe^{3+}_{(1)}$	789 ± 226	0.29 ± 0.07	1.39 ± 0.18	0.94 ± 0.32	90
	$Fe^{3+}_{(2)}$	85 ± 96	0.35 ± 0.07	0.40 ± 0.11	0.26 ± 0.18	10
b.)	$Fe^{3+}_{(1)}$	722 ± 217	0.28 ± 0.04	1.62 ± 0.11	0.50 ± 0.16	51
	$Fe^{3+}_{(3)}$	611 ± 154	0.33 ± 0.04	0.59 ± 0.07	0.48 ± 0.08	49

FIGURE 5. The Mössbauer spectrum of ^{57}Fe in the sample ZMV 7 – brown layer at room temperature
I – $Fe^{3+}_{(1)}$ - tetrahedral sites, II – $Fe^{3+}_{(3)}$ - octahedral sites, IV – Fe^{2+}

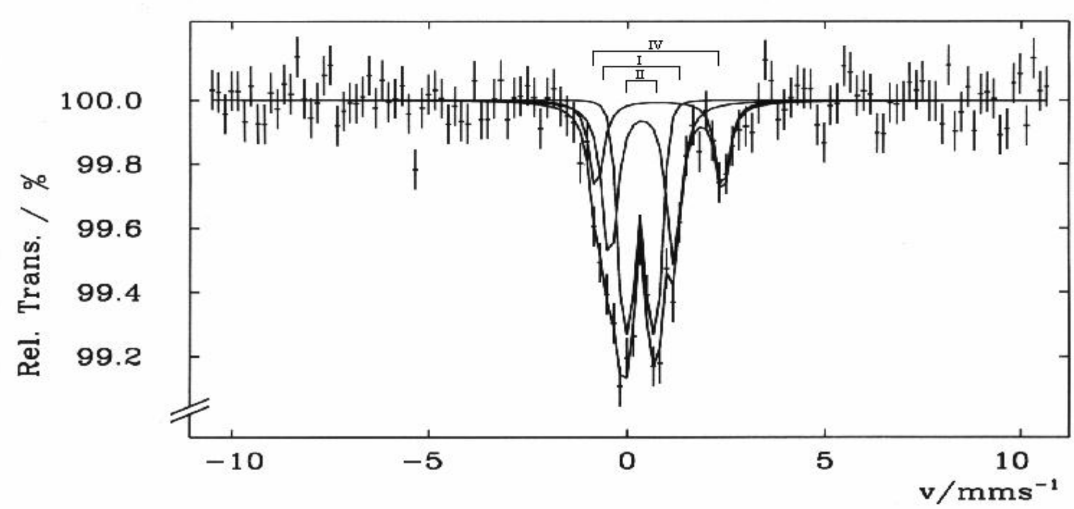


TABLE 19. Hyperfine parameters of Mössbauer spectrum of the sample ZMV 7 at room temperature
a.) undamaged plaster
c.) brown layer

	oxidation state	*surface area*	isomer shift δ [mm/s]	quadrupole splitting ΔE_Q[mm/s]	line width Γ [mm/s]	relative intensity [%]
a.)	$Fe^{3+}_{(1)}$	4595 ± 1036	0.28 ± 0.05	1.44 ± 0.15	0.70 ± 0.18	68
	$Fe^{3+}_{(2)}$	2152 ± 803	0.34 ± 0.05	0.43 ± 0.08	0.42 ± 0.10	32
b.)	$Fe^{3+}_{(1)}$	2762 ± 1037	0.40 ± 0.04	1.61 ± 0.12	0.40 ± 0.16	31
	$Fe^{3+}_{(3)}$	4625 ± 961	0.36 ± 0.03	0.69 ± 0.07	0.50 ± 0.08	53
	Fe^{2+}	1420 ± 588	0.85 ± 0.06	3.18 ± 0.12	0.36 ± 0.16	16

From the room temperature Mössbauer spectra it was not possible to distinguish between goethite (α-FeOOH) and ferrihydrite ($Fe_5HO_8{\cdot}4H_2O$). It is only obvious that there is a difference in chemical environment of ferric ions in brown layers and in the corresponding undamaged plaster underneath the brown layers. Therefore a low temperature spectrum (Figure 6) at 73 K was recorded for brown layer of sample DDD 36. The spectrum shows a sextet pattern as well as two overlapping doublet patterns. A hyperfine magnetic field appears because some of the particles have reached magnetic order. The linewidths are quite large. The results are shown in Table 20.

FIGURE 6. The Mössbauer spectrum of ^{57}Fe in the sample DDD 36-brown layer at temperature 73 K
I – $Fe^{3+}_{(1)}$ - tetrahedral sites, III – $Fe^{3+}_{(3)}$ - octahedral sites

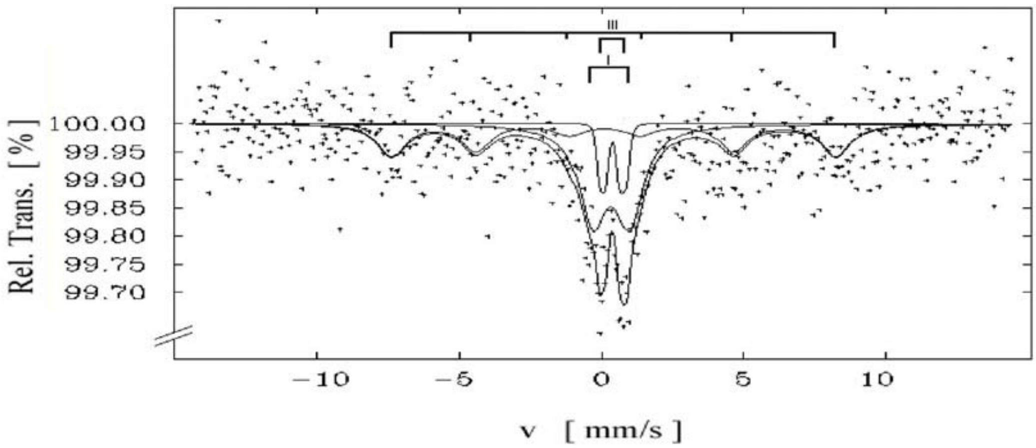


TABLE 20. Hyperfine parameters of Mössbauer spectrum of the sample DDD 36-brown layer recorded at
73 K .
a.) doublet
b.) sextet

	oxidation state	***surface area***	**isomer shift** δ [mm/s]	**quadrupole splitting** ΔE_Q [mm/s]	**line width** Γ [mm/s]	**hyperfine magnetic field** H [T]
a.)	$Fe^{3+}_{(1)}$	3402 ± 1280	0.39 ± 0.11	1.30 ± 0.61	1.18 ± 0.38	/
	$Fe^{3+}_{(3)}$	958 ± 1392	0.46 ± 0.06	0.72 ± 0.16	0.44 ± 0.26	/
b.)	$Fe^{3+}_{(3)}$	2653 ± 1035	0.33	− 0.63	1.12	48.6

Discussion

Samples of brown layers and samples of corresponding undamaged plaster underneath consist of elements: Ca, Si, Al, Mg, K, S, Fe, Ti, O, C, H.

The DTA endothermic effect at 100 °C (Figure 1) can be ascribed to the desorption of surface bound water. A slow, continuous mass loss in the temperature range of 100-500 °C is a characteristic of OH group polycondensation. A significant mass loss in the temperature range of 600-900 °C belongs to the degradation of carbonates.[7] In samples DDD 36-undamaged plaster (Figure 2) and ZMV 7-undamaged plaster are present both $CaCO_3$ and $CaMg(CO_3)_2$. On account of that the degradation of carbonates occurs in two steps. $CaMg(CO_3)_2$ decomposes in the temperature range of 400-700 °C.[7]

The IR spectra confirm conclusions from the TG analysis. A broad band (sample DDD 36-brown layer) in the range of 3700-3000 cm^{-1} can be assigned to vibrations of water.[8] Since the band is broad it can be assumed that molecules of water are differently bound to metals present in the sample. In the residual after TG analysis broad band in this area disappears and the sharp band at 3640 cm^{-1} can be ascribed to stretching mode of O-H group.[8] It appears due to partial hydration of metal oxides on air after TG analysis. Strong, broad band in the range of 1500-1400 cm^{-1} and two sharp peaks at 873 cm^{-1} and 713 cm^{-1} belong to $–CO_3$ modes.[8] The first one is significant for ν_3(C–O) stretching modes, the second one can be ascribed to π modes of the whole carbonate group and the last one to ν_4(O–C–O) bending modes. These bands are missing in the spectrum taken on the rest after TG analysis. The broad band in the range of 1200 – 800 cm^{-1} appears in both spectra and can be ascribed to M – O modes[8] of various metal oxides present in samples. Because IR spectra didn't give the information which metal oxides are present, we didn't record spectra of all samples.

Components which show the best matching of lines in X-ray powder patterns are $CaCO_3$, SiO_2, Ca_2SiO_4, $CaMg(CO_3)_2$, silicate minerals containing Ca, Al, Mg, K, Fe, metal hydroxides and sulphates. It was possible to determine more components in residuals after TG analysis. In addition to better crystallised phases, e.g. SiO_2, a number of new phases appeared in residuals due to chemical reactions.

From the above analyses it could not be concluded that iron is involved in chemical changes of external layers of building facades. Mössbauer analysis turned out to be a convenient method for investigation of iron in poorly crystalline material.

Two overlapping doublet patterns (Figure 3) in the room temperature spectra of undamaged plaster of the sample DDD 36 can be ascribed to ferric ions on tetrahedral ($\mathbf{Fe^{3+}_{(1)}}$) and octahedral ($\mathbf{Fe^{3+}_{(2)}}$) sites in ferrites of brownmillerite-like structure [2]. In brown layers coordination remains tetrahedral and octahedral ($\mathbf{Fe^{3+}_{(3)}}$), but there are more ferric ions at octahedral sites what can be concluded by comparing relative intensities (Table 18 and 19). The change in quadrupole splitting parameter of about 0.2 mm/s indicates a change in chemical environment of the octahedrally coordinated ferric ions ($\mathbf{Fe^{3+}_{(3)}}$). Parameters of $Fe^{3+}_{(3)}$ agree well with parameters of microcrystalline goethite (α-FeOOH)[9] and ferrihydrite ($Fe_5HO_8{\cdot}4H_2O$).[3,9] To determine which one of these two minerals is present in brown layers the low temperature spectrum at 73 K was recorded (Figure 6). Parameters of this spectrum (Table 20) match with parameters of microcrystalline goethite.[9] The hyperfine magnetic field is 1 T lower than that found in literature, which can be explained by aluminium substitution, sample crystallinity and particle size effects.[10,11] The difference between brown layers and undamaged plaster underneath the brown layers is in formation of goethite (α-FeOOH). It is microcrystalline and some of the Fe^{3+} ions are substituted by a non magnetic ion, probably Al^{3+}.

Iron in oxidation state 2+ is present only in the brown layer of sample ZMV 7 (Figure 5). One of the possible ways of its genesis is reduction of Fe^{3+} due to SO_2 present in the air.

Acknowledgements

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References and Notes

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Povzetek

Na nekaterih arheoloških stavbah je fasada tik pod površino rjavo obarvana. Ta rjava obarvanost je posledica kemijskih sprememb, ki lahko pozročijo tudi nadaljno destrukcijo fasade.

Rjavo plast in nepoškodovano plast fasade tik pod rjavo plastjo sestavljajo $CaCO_3$, SiO_2, Ca_2SiO_4, $CaMg(CO_3)_2$, silikati, ki vsebujejo Ca, Al, Mg, K, Fe, kovinski hidroksidi in sulfati. V obeh plasteh je tudi nekaj površinsko vezane vode. Fe^{3+} ioni so tetraedrično in oktaedrično koordinirani. V rjavi plasti je več Fe^{3+} ionov na oktaedričnih mestih in eksperimentalni podatki kažejo tudi na spremembo kemijskega okolja Fe^{3+} ionov. Razlika med rjavo plastjo in nepoškodovano plastjo fasade je v tem, da je v rjavi plasti nastal goethit (α - FeOOH), ki je mikrokristaliničen in delež Fe^{3+} ionov je substituiran z ne – magnetnim ionom, verjetno Al^{3+} ionom. Železo v oksidacijskem stanju 2+ je prisotno samo v rjavi plasti vzorca ZMV 7. Ena od možnih poti nastanka je z redukcijo Fe^{3+}, zaradi prisotnosti SO_2 v zraku.