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FRANK LABORATORY OF NEUTRON PHYSICS

Study of the wall painting from the Vladychinaya palata of the Novgorod kremlin (Velikiy Novgorod, Russia) using complementary physico-chemical methods

V.V. Lobachev[1], A.Yu. Dmitriev[1], O.S. Philippova[1], S.G. Lennik[1,2], N.V. Lobacheva[1]

[1] *Joint Institute for Nuclear Research, Dubna, Russia*

[2] *Institute of Nuclear Physics, Almaty, Kazakhstan*

Outline

- Introduction and objectives
- Study of plasters
- Study pigment composition in paint layers
- Conclusions

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Vladychinaya palata

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1. The UNESCO World Heritage Site;
2. It was built in 1433 with the participation of German masters, in the Western European Gothic style;
3. It served as the meeting place of the council of nobility and the boyar court of the Novgorod republic;
4. Interior decorated with 15^{th}-19^{th} century wall painting.

Wall painting fragments

Research objective

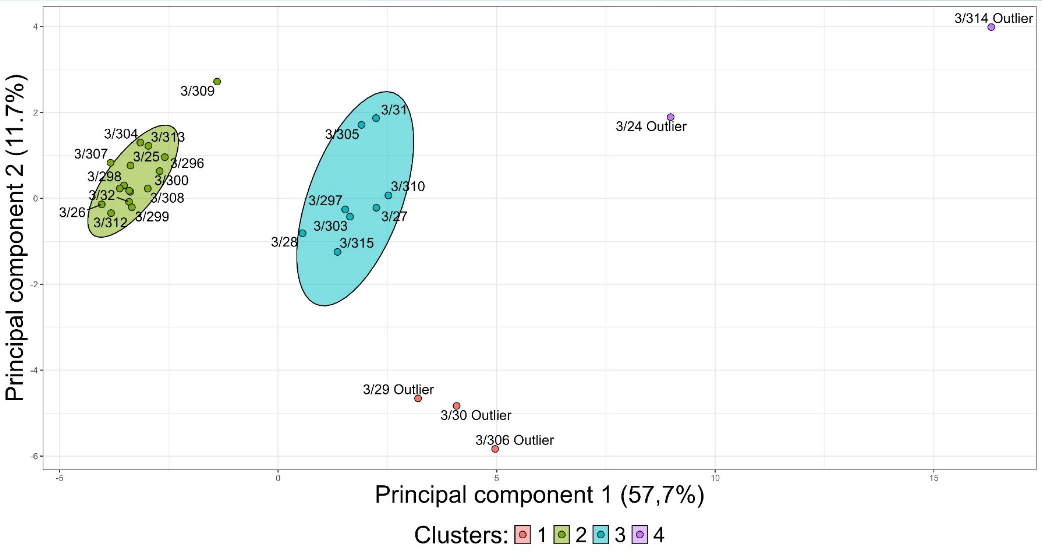
Comprehensive study of the wall painting fragments in the Vladychinaya palata of the Novgorod kremlin using complementary physico-chemical methods

Tasks

1. Study the elemental composition of plasters;
2. Check the possibility of grouping samples by elemental composition using multivariate mathematical statistics methods;
3. Study the pigment composition of paint layers;
4. Carry out a comprehensive description of the samples based on elemental and pigment analysis.

Study methods

1. Neutron activation analysis (NAA);
2. K-means and PCA methods;
3. X-ray fluorescence analysis (XRF);
4. Stratigraphic analysis;
5. Optical and polarized microscopy;
6. Raman spectroscopy.



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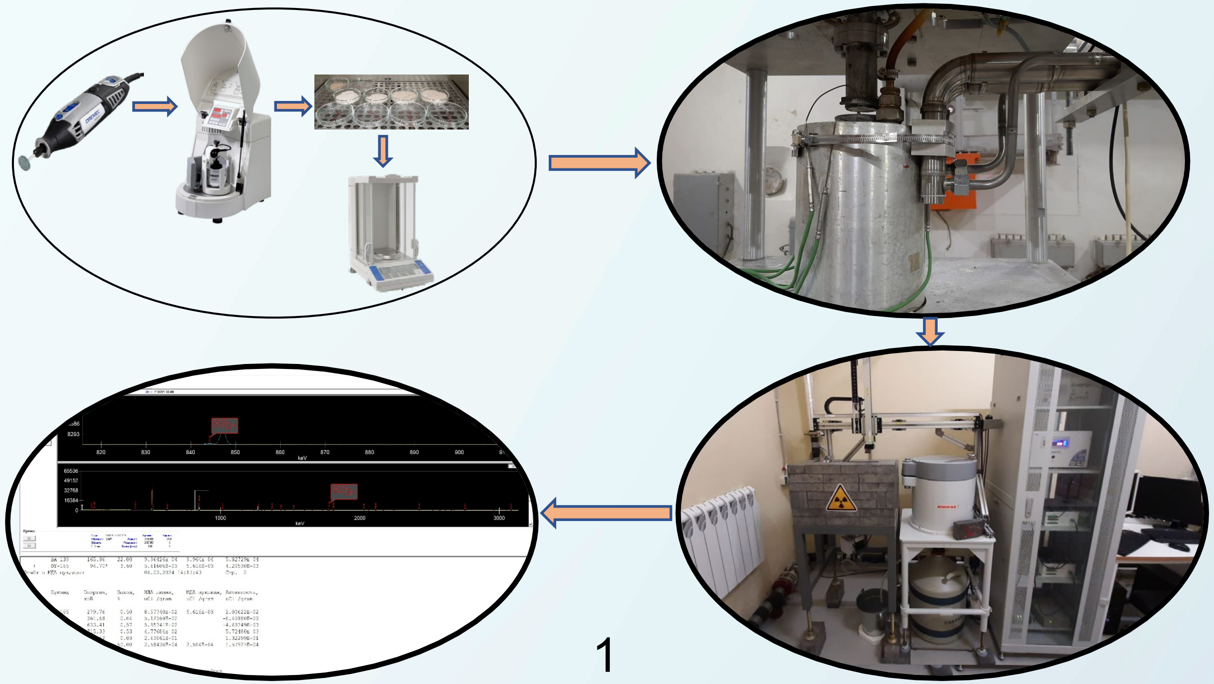

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Radiation exposure parameters

WWR-K reactor “Dry” channel for short-lived isotopes:

Neutron flux:

- thermal: 4.4 * 10^{12} n / cm²s;
- resonance: 3.8 * 10^{10} n / cm²s.

Weight of samples:

- 0.1 grams

Irradiation time:

- 1 minute

WWR-K reactor “Wet" channel for long-lived isotopes:

Neutron flux:

- thermal: 6.6 * 10^{13} n / cm²s;
- resonance: 3.0 * 10^{12} n / cm²s.

Weight of samples:

- 0.1 grams

Irradiation time:

- 90 minutes

Neutron Activation Analysis

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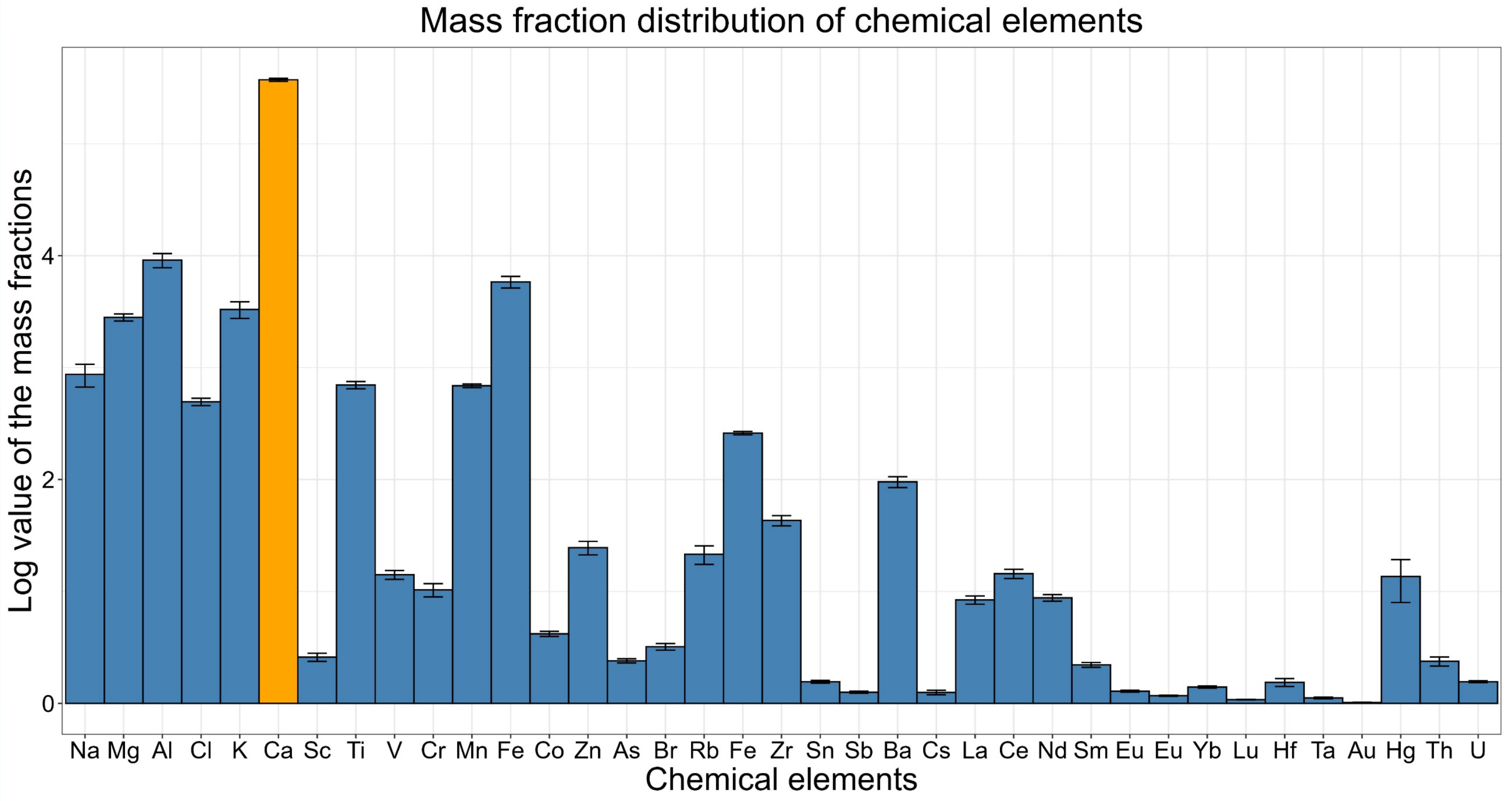
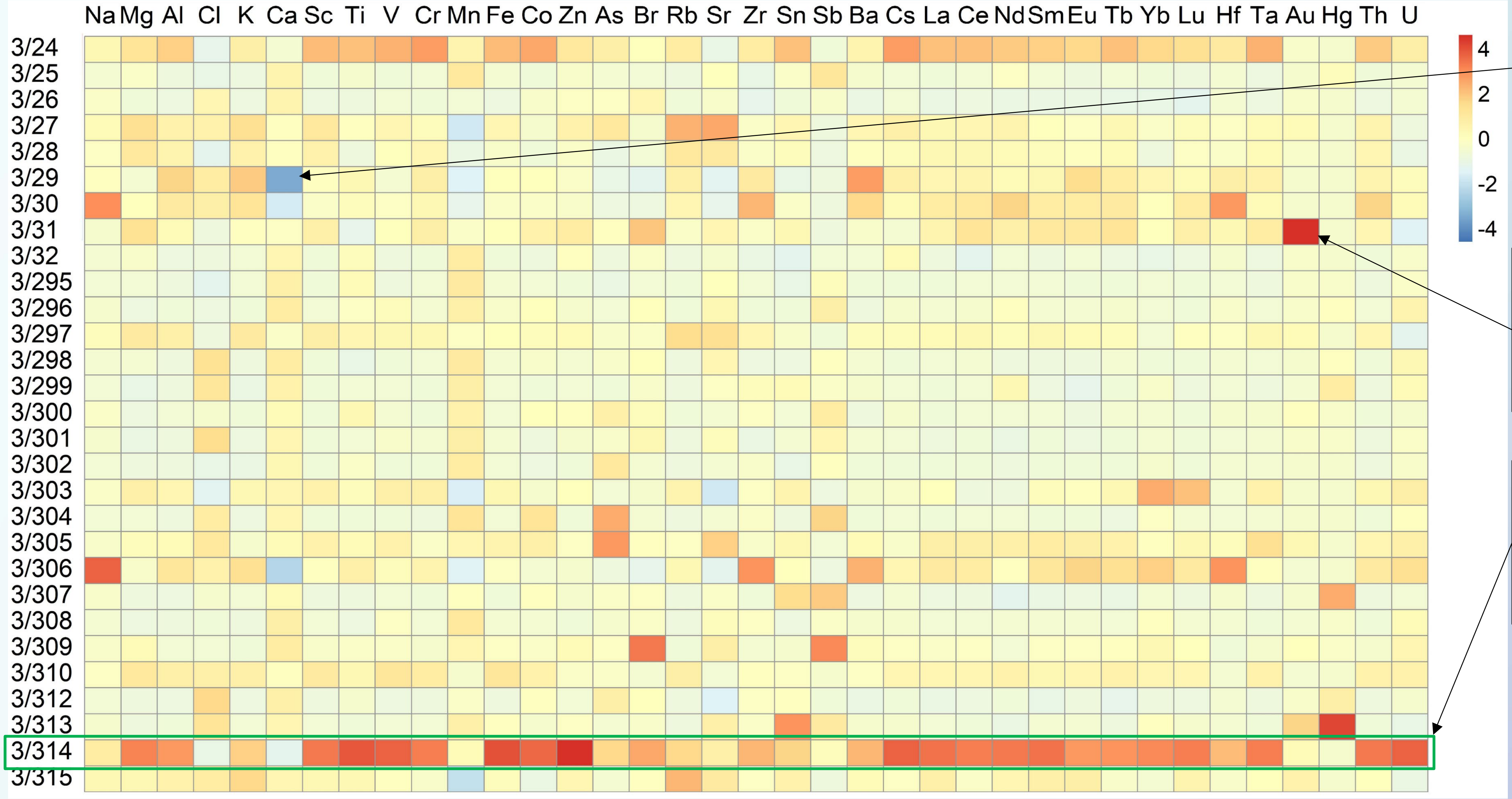
1. Relative NAA method;
2. NIST Standards: 1486, 1566B, 1632E, 1633C, 2586, 2706, 2709A, 2710A, 2780A;
3. Mass fractions of 37 chemical elements.



Element	Mean±Se	Median	Min–Max
Na	869±200	479	207–4870
Mg	2810±203	2430	1640–6250
Al	9130±1330	4580	2610–29000
Cl	494±37.5	410	217–820.
K	3310±562	1480	442–9120
Ca	**373000±11700**	**397000**	**157000–429000**
Sc	1.58±0.216	0.915	0.551–5.47
Ti	698±52.1	656	384–1800
V	13.1±1.27	11.5	7.20–38.6
Cr	9.33±1.39	5.52	3.70–34.04
Mn	687±26.4	750	398–865
Fe	5830±692	4700	2740–20900
Co	3.17±0.218	2.79	2.08–7.40
Zn	23.6±3.39	19.4	10.3–108
As	1.39±0.102	1.20	0.825–2.94
Br	2.20±0.219	1.94	0.714–6.15
Rb	20.5±4.05	5.45	2.67–71.5
Sr	259±9.18	262	172–383
Zr	42.1±4.50	37.0	15.2–113
Sn	0.552±0.0458	0.499	0.253–1.27
Sb	0.249±0.0290	0.196	0.108–0.724
Ba	94.3±10.6	70.8	40.7–250
Cs	0.243±0.0587	0.109	0.0317–1.42
La	7.40±0.714	5.35	3.75–20.6
Ce	13.4±1.36	9.37	4.32–37.6
Nd	7.76±0.593	7.45	3.80–18.4
Sm	1.20±0.109	0.904	0.59–3.23
Eu	0.277±0.0255	0.209	0.115–0.669
Tb	0.163±0.0137	0.130	0.0805–0.375
Yb	0.392±0.0301	0.340	0.220–0.887
Lu	0.0711±0.00606	0.0566	0.0301–0.179
Hf	0.532±0.126	0.223	0.0664–2.52
Ta	0.110±0.0179	0.0660	0.0254–0.427
Au	0.00883±0.00225	0.0049	0.00239–0.0645
Hg	12.6±5.64	1.14	0.134–140
Th	1.37±0.222	0.667	0.377–5.33
U	0.552±0.0289	0.514	0.330–1.14

Heatmap of element mass fractions



Low mass fraction of Ca in sample 3/29

High mass fraction of Au in sample 3/31

High mass fractions of most elements in sample 3/314

Outlier detection

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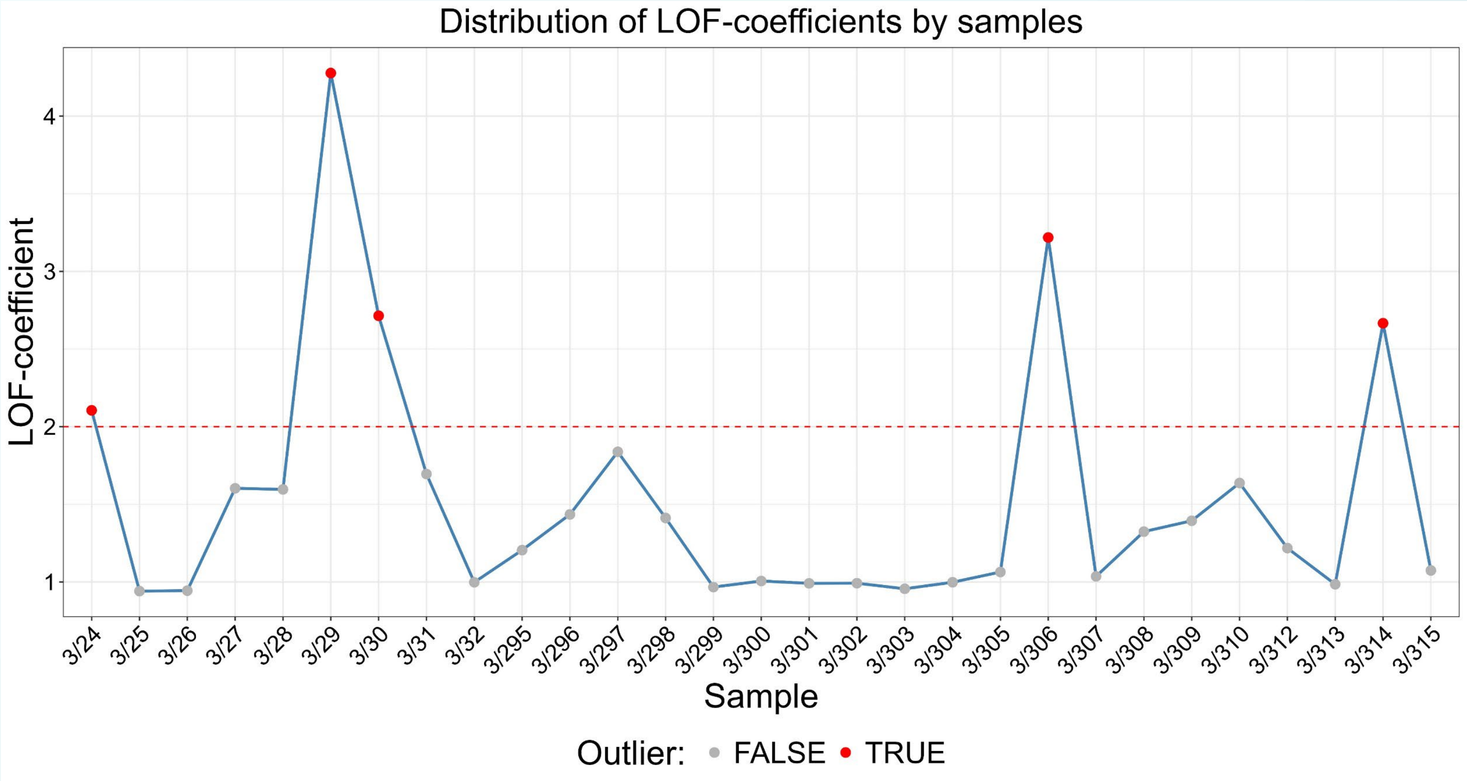
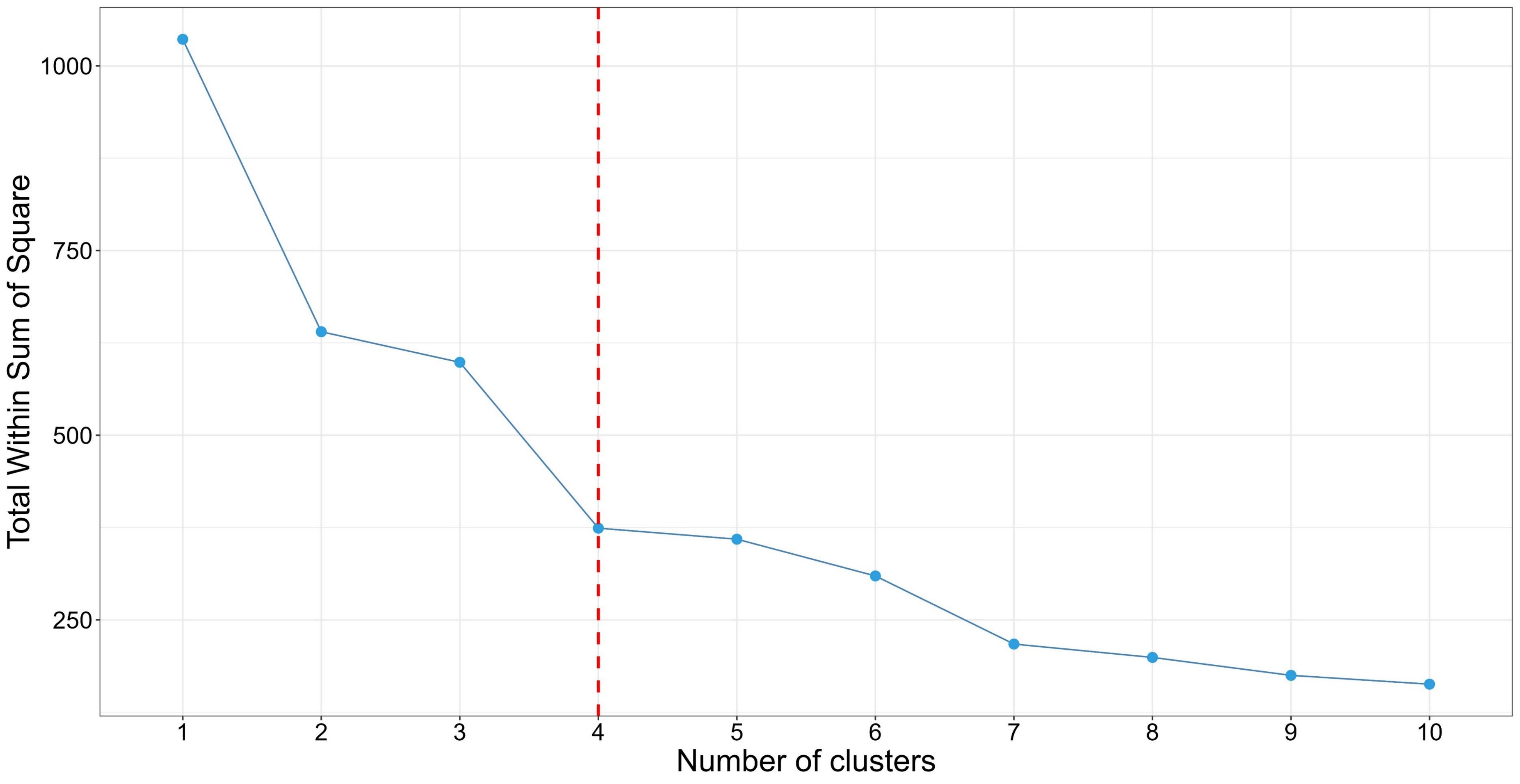
1. Shapiro-Wilk and Henze-Zirkler tests: data aren't normally distributed;
2. Local Outlier Factor (LOF) method: outlier detection without distribution assumptions;
3. LOF-coefficient > 2 - optimal balance for outlier detection;
4. Detected outliers: 3/24, 3/29, 3/30, 3/306, 3/314.



Sample	LOF-coefficient	Outlier
3/24	2.105	TRUE
3/25	0.941	FALSE
3/26	0.944	FALSE
3/27	1.603	FALSE
3/28	1.596	FALSE
3/29	4.277	TRUE
3/30	2.714	TRUE
3/31	1.695	FALSE
3/32	0.998	FALSE
3/295	1.205	FALSE
3/296	1.435	FALSE
3/297	1.838	FALSE
3/298	1.412	FALSE
3/299	0.967	FALSE
3/300	1.006	FALSE
3/301	0.991	FALSE
3/302	0.992	FALSE
3/303	0.956	FALSE
3/304	0.998	FALSE
3/305	1.064	FALSE
3/306	3.218	TRUE
3/307	1.036	FALSE
3/308	1.324	FALSE
3/309	1.394	FALSE
3/310	1.637	FALSE
3/312	1.218	FALSE
3/313	0.985	FALSE
3/314	2.666	TRUE
3/315	1.074	FALSE

Optimal cluster number determination



PCA method for cluster visualization

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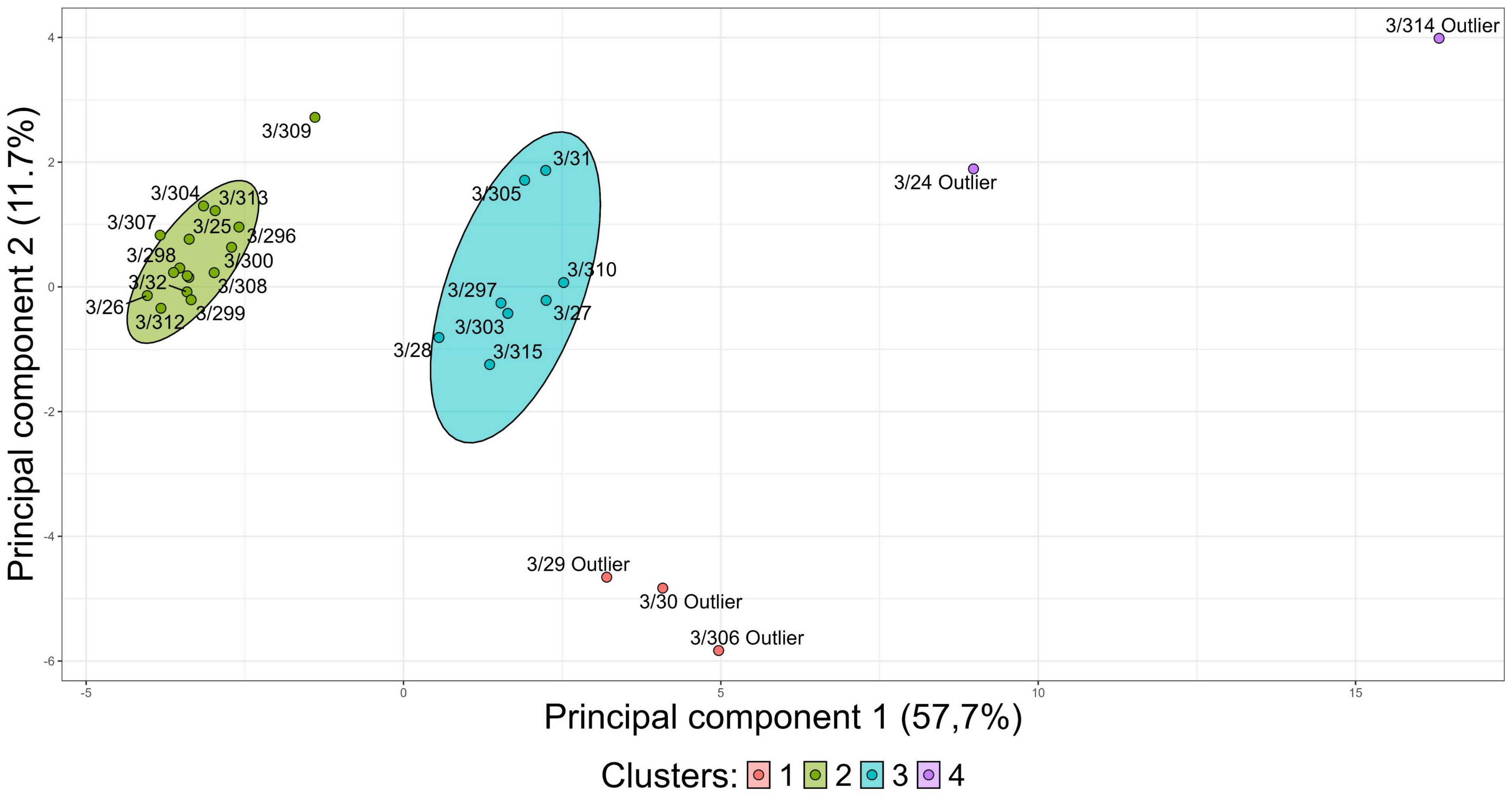

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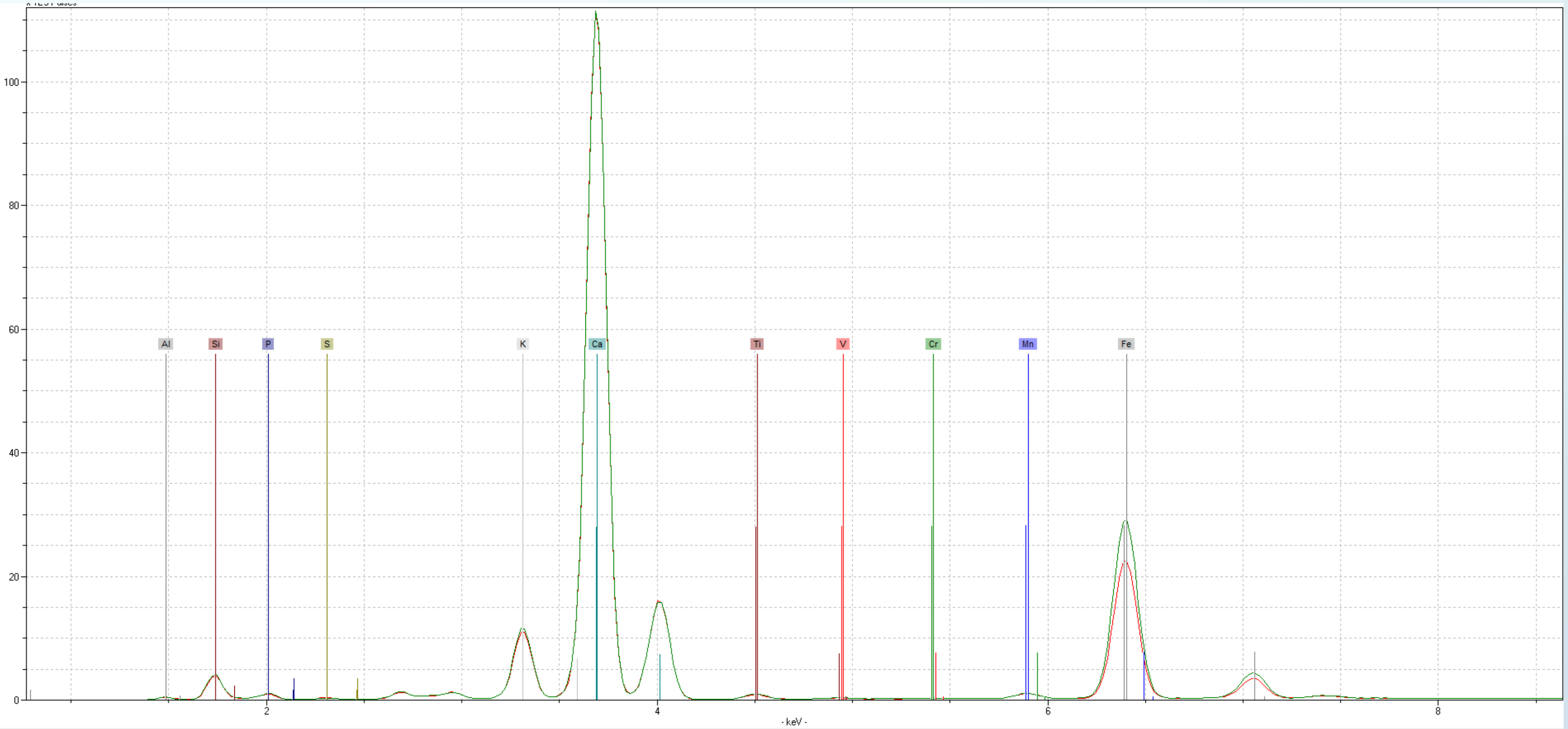
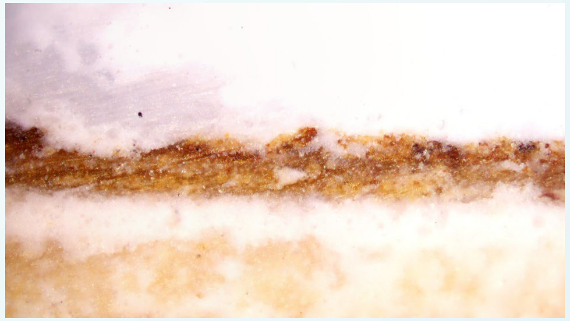
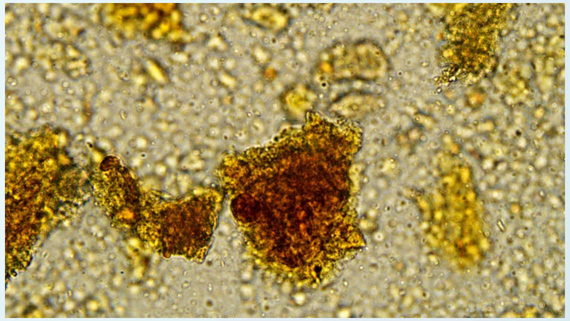
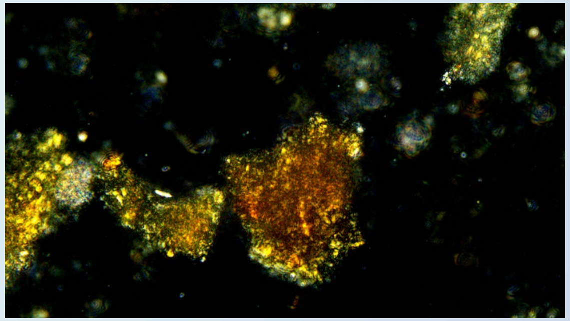
Methods for studying pigment composition

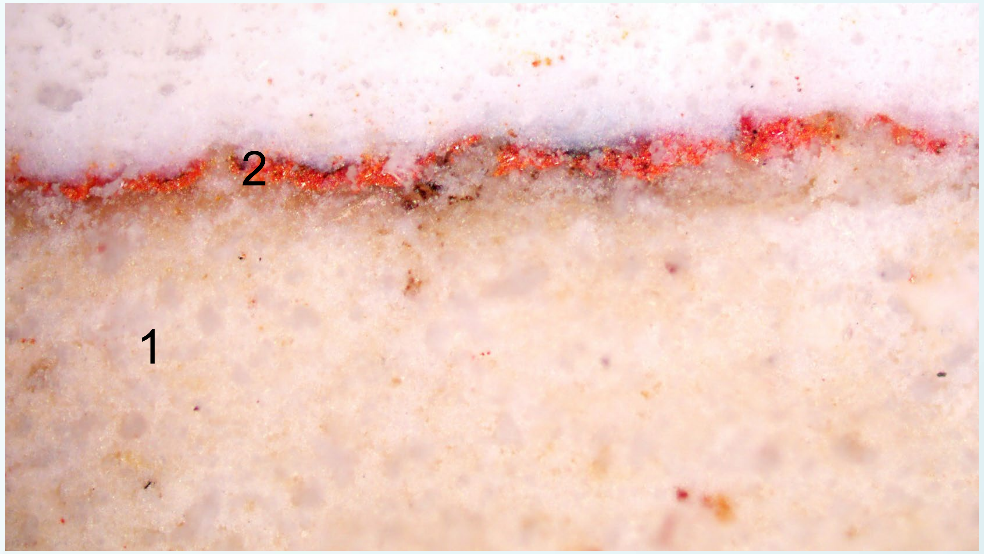


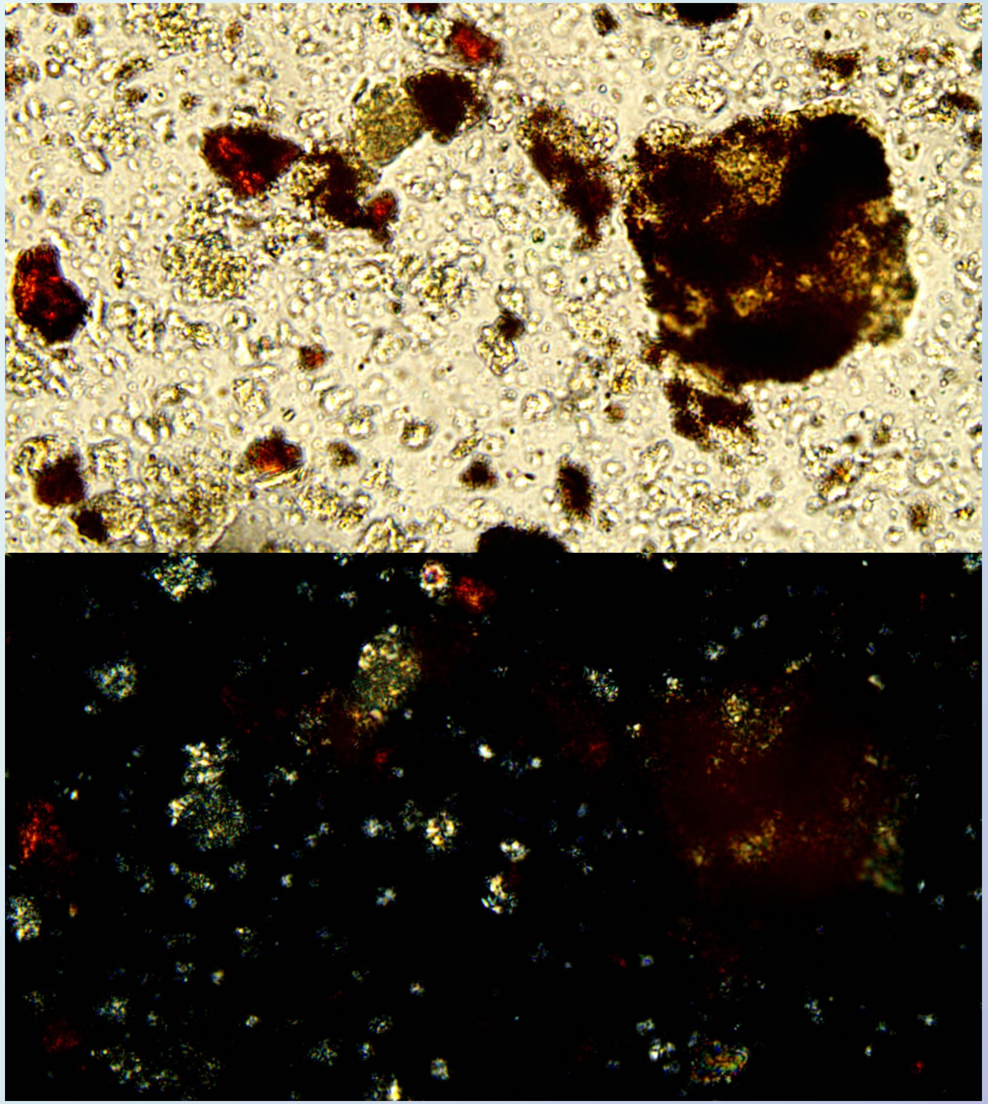






Red paint layer





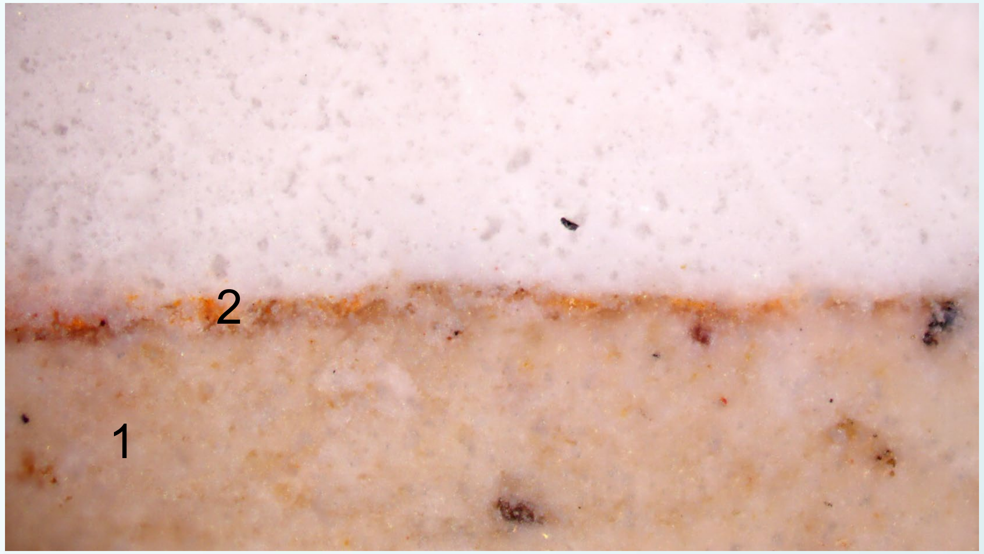
2. Red paint layer with black inclusions
1. Plaster

Color	Characteristic elements
Red	Al, Si, **Hg**, K, **Ca**, Ti, **Mn**, **Fe**

Pigments:

- Red ochre (Fe_2O_3)
- Cinnabar (HgS)
- Carbon black (C)

Orange paint layer

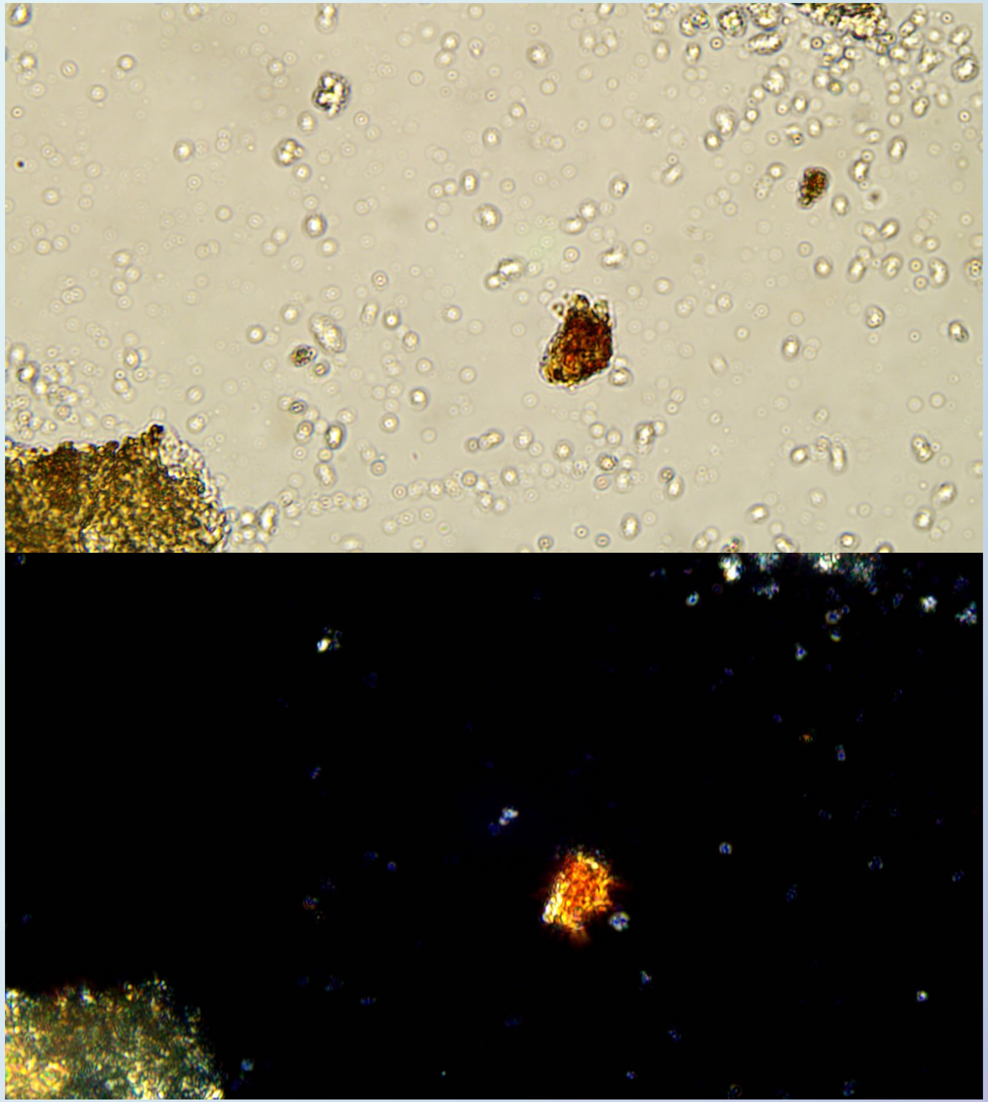


2. Orange paint layer
1. Plaster

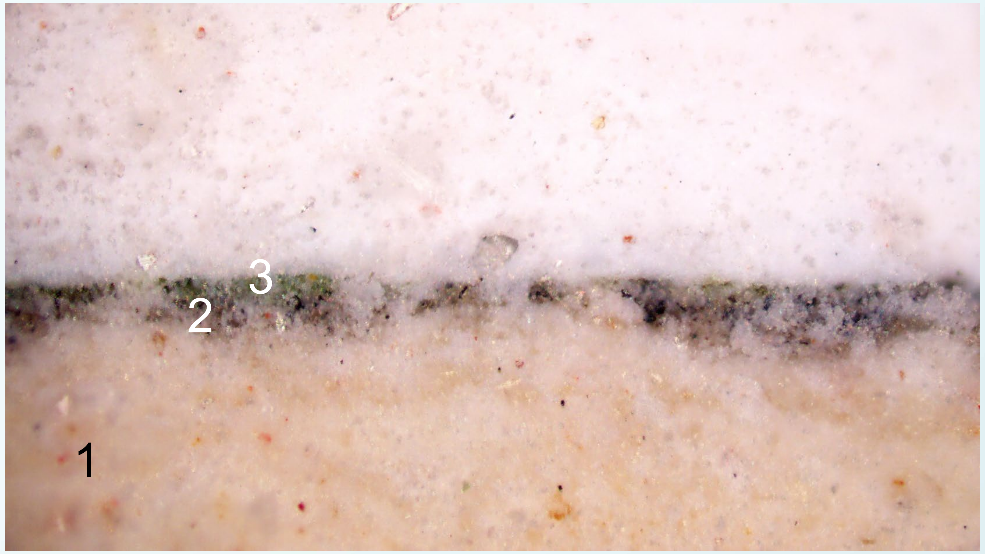
Color	Characteristic elements
Orange	Al, Si, **Pb**, K, Ca, Ti, Mn, Fe

Pigments:

- Red lead (Pb_3O_4)



Green paint layer

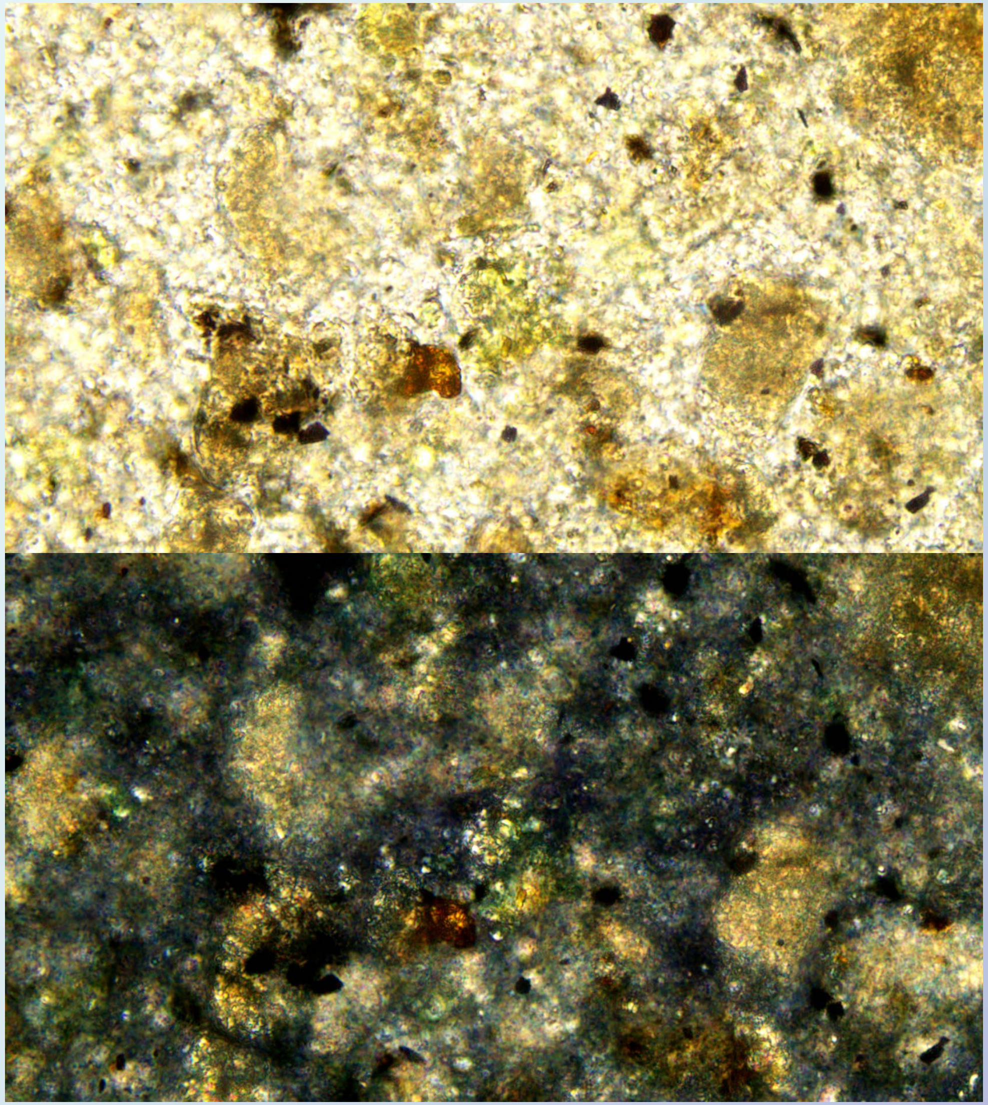


3. Green paint layer
2. Black paint later (Reft)
1. Plaster

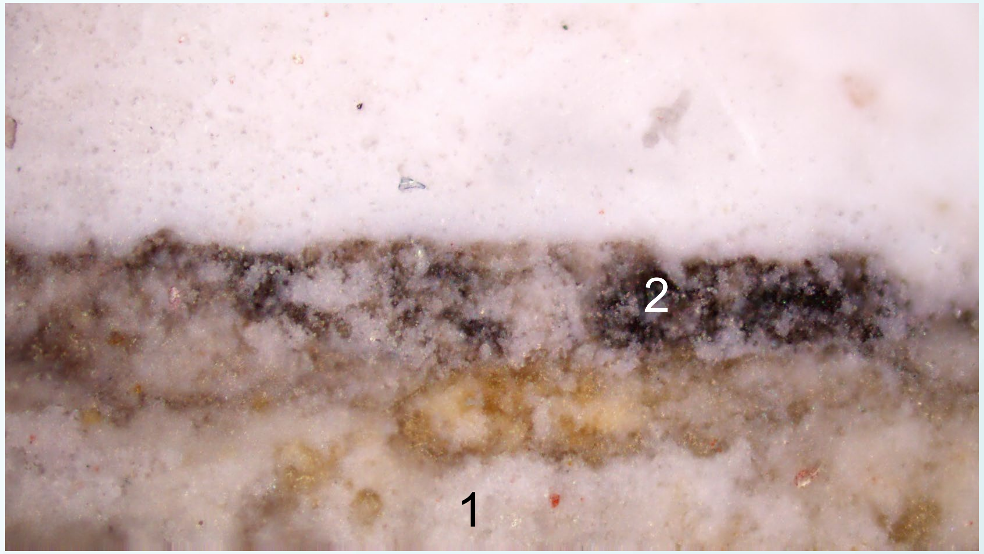
Color	Characteristic elements
Dark green	**Al**, **Si**, S, **K**, Ca, Ti, Mn, **Fe**

Pigments:

- Green earth $(Si_{4x}Al_x)_4(Fe^{3+},Fe^{2+},Al,Mg)_2O_{10}(OH)_2K_{(x+y)}$
- Carbon black (C)



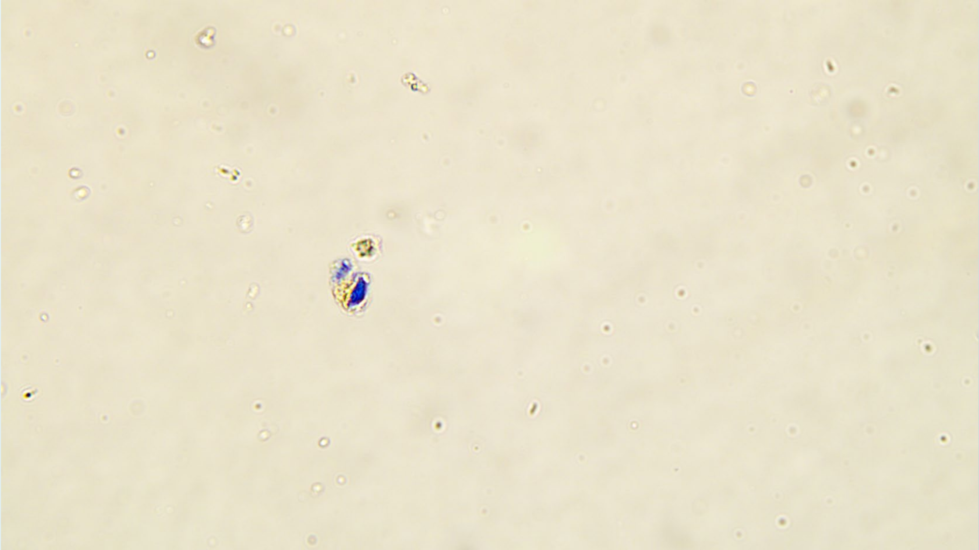
Black paint layer with fragmentary preserved blue layer

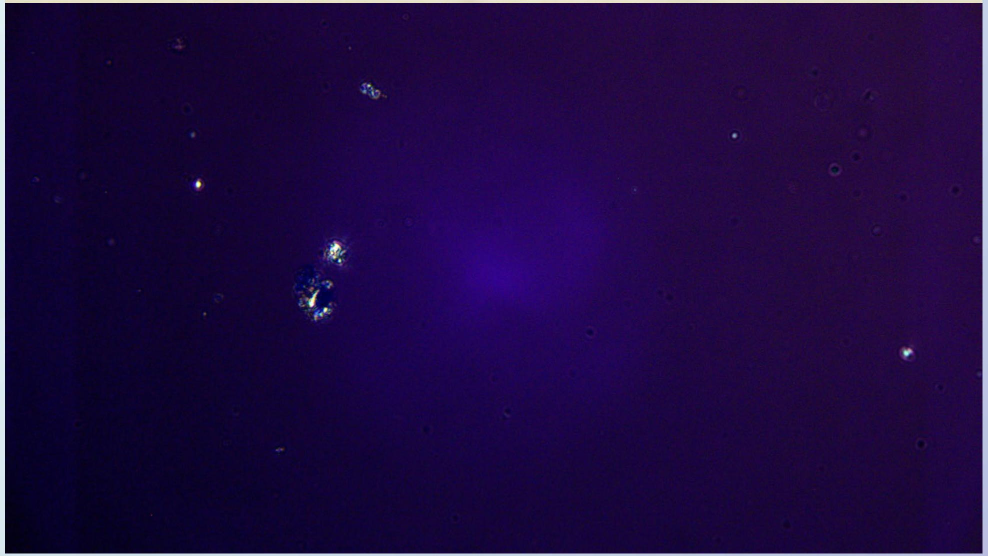


2. Grey paint layer
1. Plaster

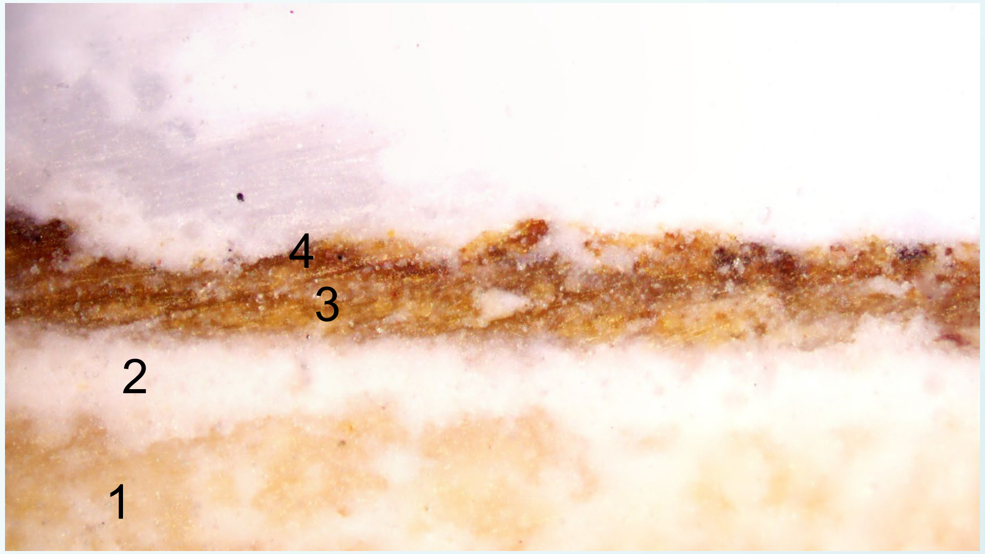
Color	Characteristic elements
Grey	Al, **Si**, S, K, Ca, Ti, Mn, Fe

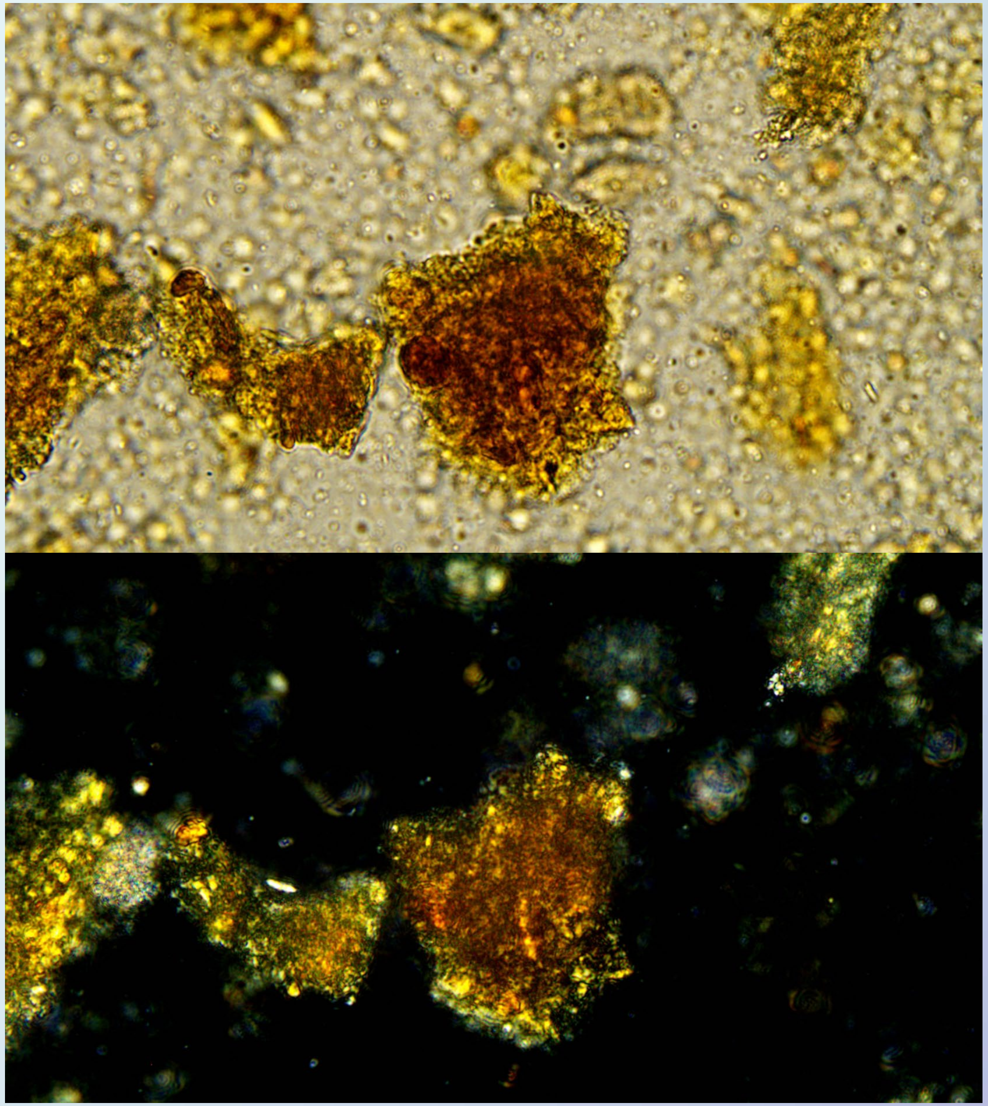
Pigment:
- Carbon black (C)
- Lime white ($CaCO_3$)
- Lazurite $(Na,Ca)_8[(Al,Si)_{12}O_{24}](S,SO_4)$





Yellow paint layer



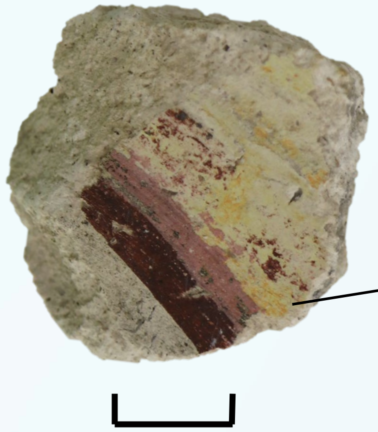


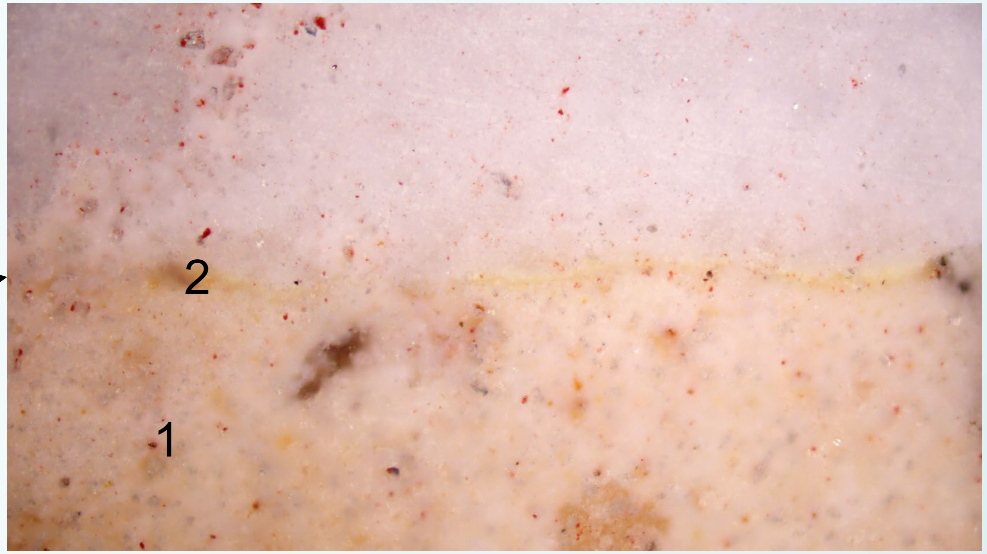
4. Dark yellow paint layer
3. Yellow paint layer
2. White paint layer
1. Plaster

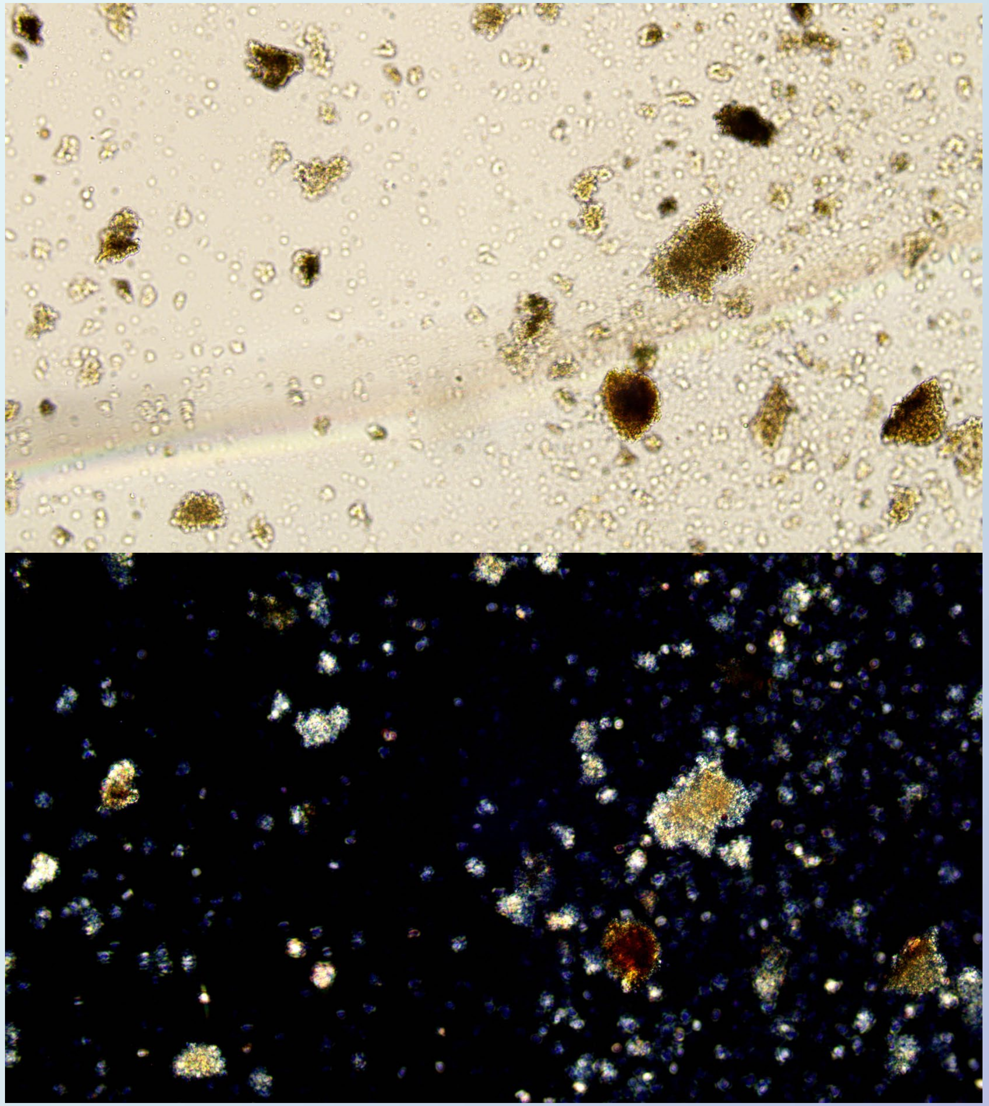
Color	Characteristic elements
Yellow	Al, **Si**, **P**, **S**, **K**, Ca, **Ti**, V, **Mn**, **Fe**

Pigment:
- Yellow ochre ($FeO(OH)$)
- Lime white ($CaCO_3$)

Interesting case







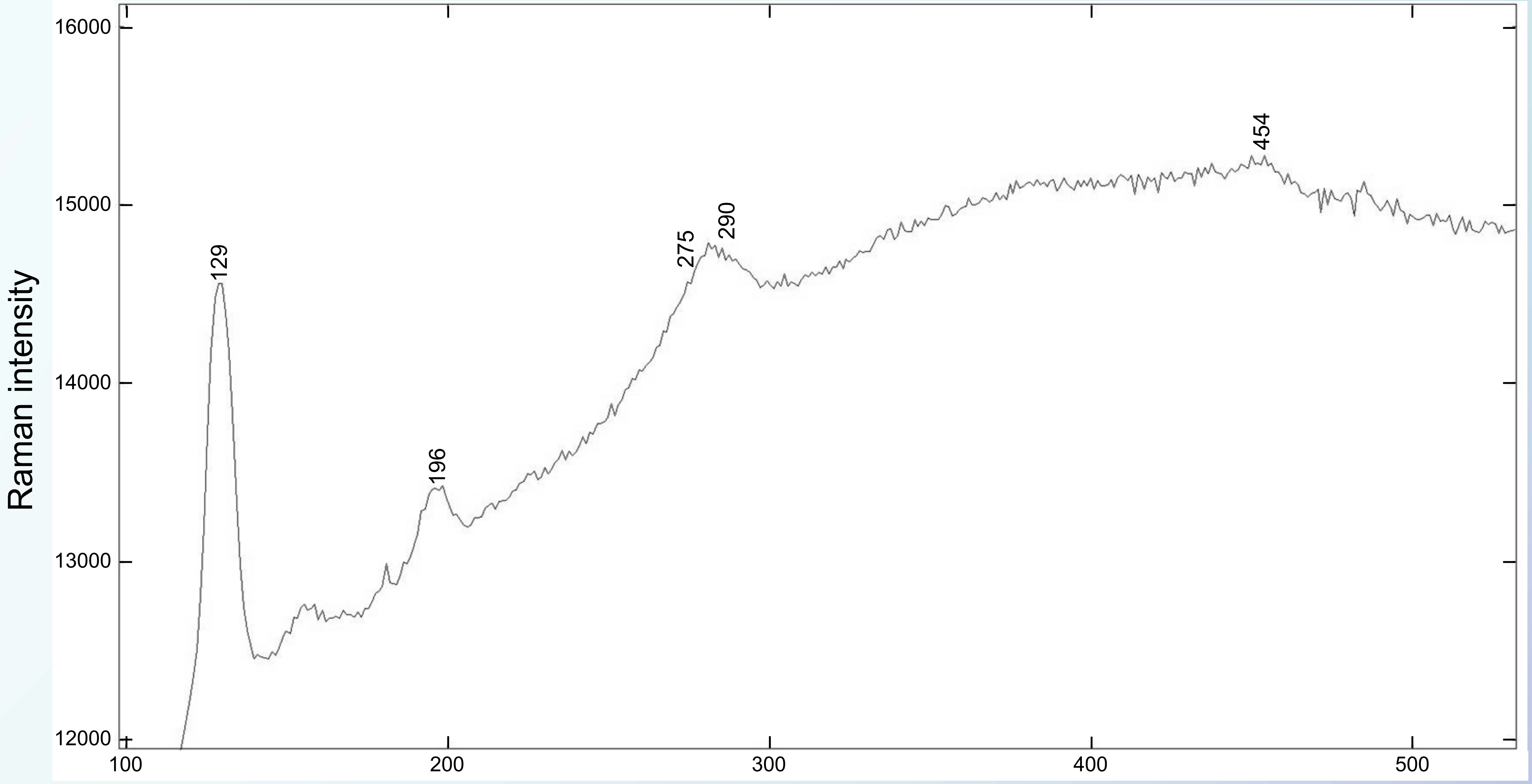
2. Yellow paint layer
1. Plaster

Color	Characteristic elements
Yellow	Al, Si, **Pb**, **Sn**, Ca, Mn, Fe

Pigment:

- Lead-tin yellow I (Pb_2SnO_4)

Lead-tin yellow I



Raman shift, cm^{-1}

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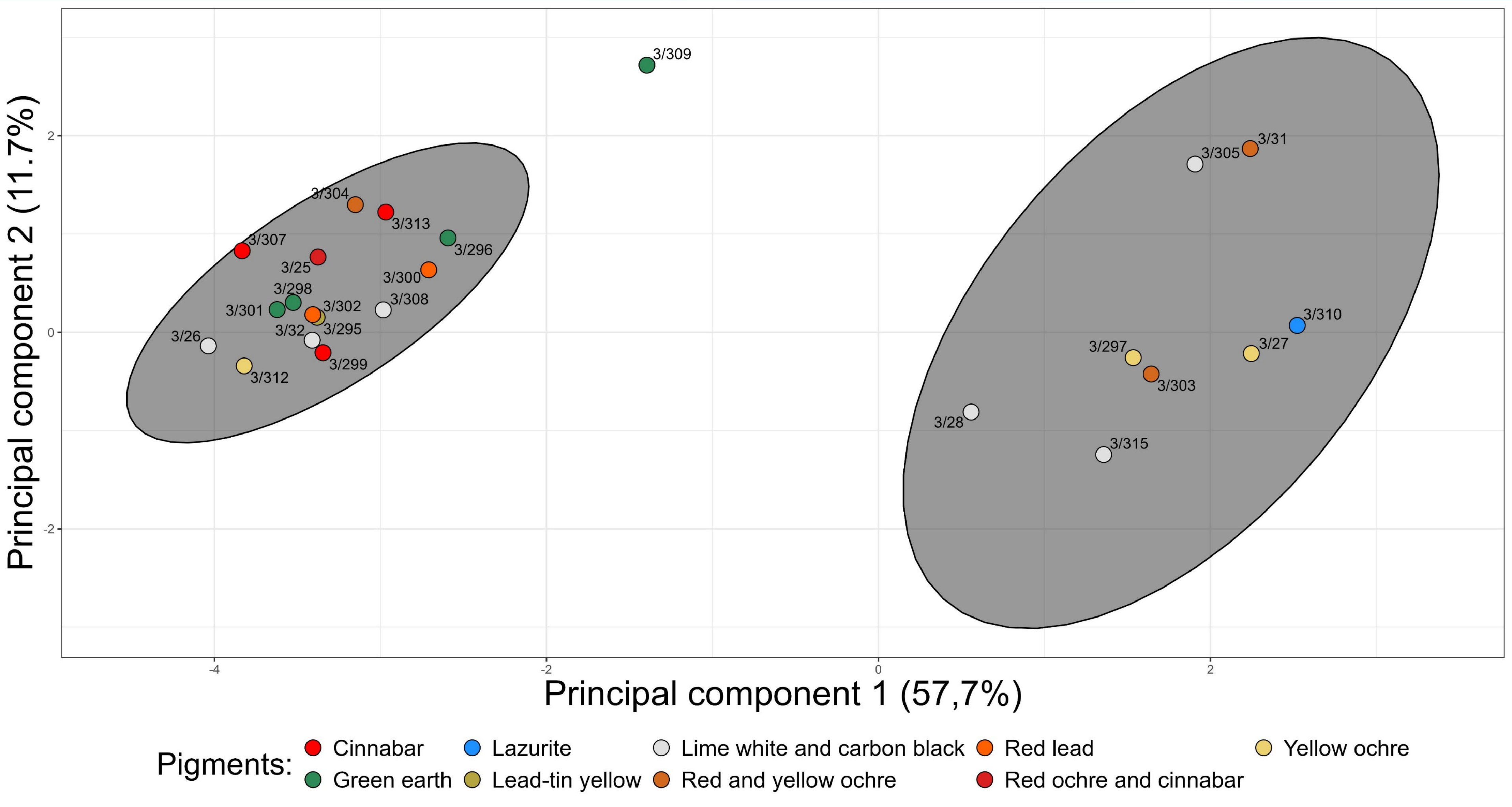
PCA method for cluster visualization with pigment color-coding



Thank you for your attention!

Histogram of LOF-coefficients distribution