University of Applied Sciences

Department of Conservation and Restoration

Science Laboratory

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Church of the Virgin (Gelati)
Salt analyses – Part I

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Introduction

11 salt samples from surfaces of the Church of the Virgin (Gelati monastery complex) were sent to the Science Laboratory of FHP with the request for analysis. The samples were taken on December 19, 2023 and documented by the restoration team.

Analytical methods

The salts were observed with a Motic SMZ-160 stereo microscope, partly using a Moticam S1 for documentation. Additional digital images were made with a Olympus DP28 digital camera on a BX51 microscope using dark field reflected light (DF) or polarized transmitted light (II-pol in oil).
The salts were determined by using X-ray diffractometry (XRD): Empyrean X-ray diffractometer from Malvern Panalytical, operative conditions: CuKα radiation, 40KV, 40mA, $2\Theta = 3\text{-}70°$. Salts with a concentration of approx. < 2% cannot be detected.

Results

The results are summarized in Table 1 and then documenting the results.

Table 1: Sample ID, location, and results of the XRD measurements, (+) = main salt, (-) = to a lower degree

Sample ID	Location	Crystallized Salts
1	E5	niter [KNO_3] (+), aphtitalite [$K_3Na(SO_4)_2$] (-)
2	E5	niter (+), picromerite [$K_2Mg(SO_4)_2 \cdot 6H_2O$], syngenite [$K_2Ca(SO_4)_2 \cdot H_2O$] (-)
3.1	E5	dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$] (+), gypsum [$CaSO_4 \cdot 2H_2O$] (-)
3.2	E5	dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$] (+), gypsum [$CaSO_4 \cdot 2H_2O$] (-)
4	E5	hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$] (+), dypingite (-)
5	4	niter [KNO_3]
6	S14	nesquehonite [$MgCO_3 \cdot 3H_2O$] (+), dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$] (-)
7	S14	nesquehonite [$MgCO_3 \cdot 3H_2O$] (+), dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$] (-)
8	E8	niter [KNO_3] (+)
9	W5	hexahydrite [$MgSO_4 \cdot 6H_2O$] (+), gypsum [$CaSO_4 \cdot 2H_2O$] (-)
10	W5	nesquehonite [$MgCO_3 \cdot 3H_2O$] (+), dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$] (-)

Sample 1 – Location: North arm, vault, East-wall E5

Description: granular crystals (partly agglomerated to a crust) and whisker (fig. 1).

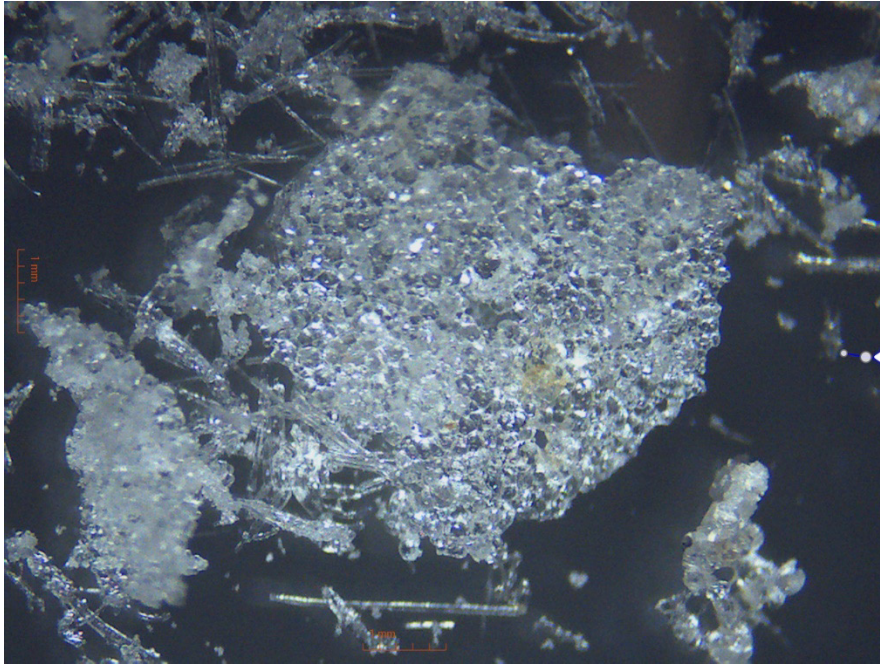Result: mostly niter [KNO_3] and to a much lower degree aphtitalite [$K_3Na(SO_4)_2$] (fig.2).

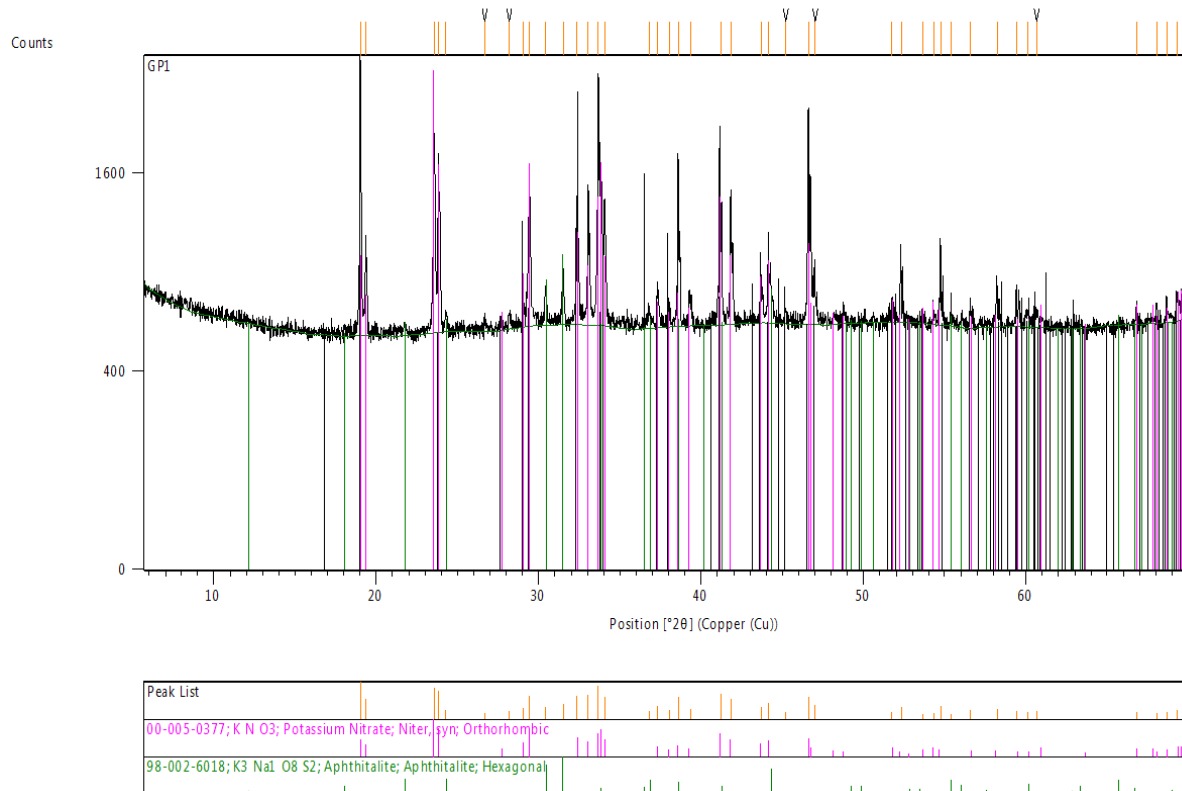fig. 1: Sample 1, granular crystals agglomerated to a crust and whiskers (Moticam S1)

fig. 2: Sample 1, XRD spectrum

Sample 2 – Location: North arm, vault, East-wall E5

Description: up to 1mm thick compact white crusts (fig. 3) consisting of transparent small crystals, similar to the agglomerated granular crystals as in sample 1.

Result by XRD: mostly niter [KNO_3], less picromerite [$K_2Mg(SO_4)_2 \cdot 6H_2O$] and to a much lower degree syngenite [$K_2Ca(SO_4)_2 \cdot H_2O$] (fig. 4).

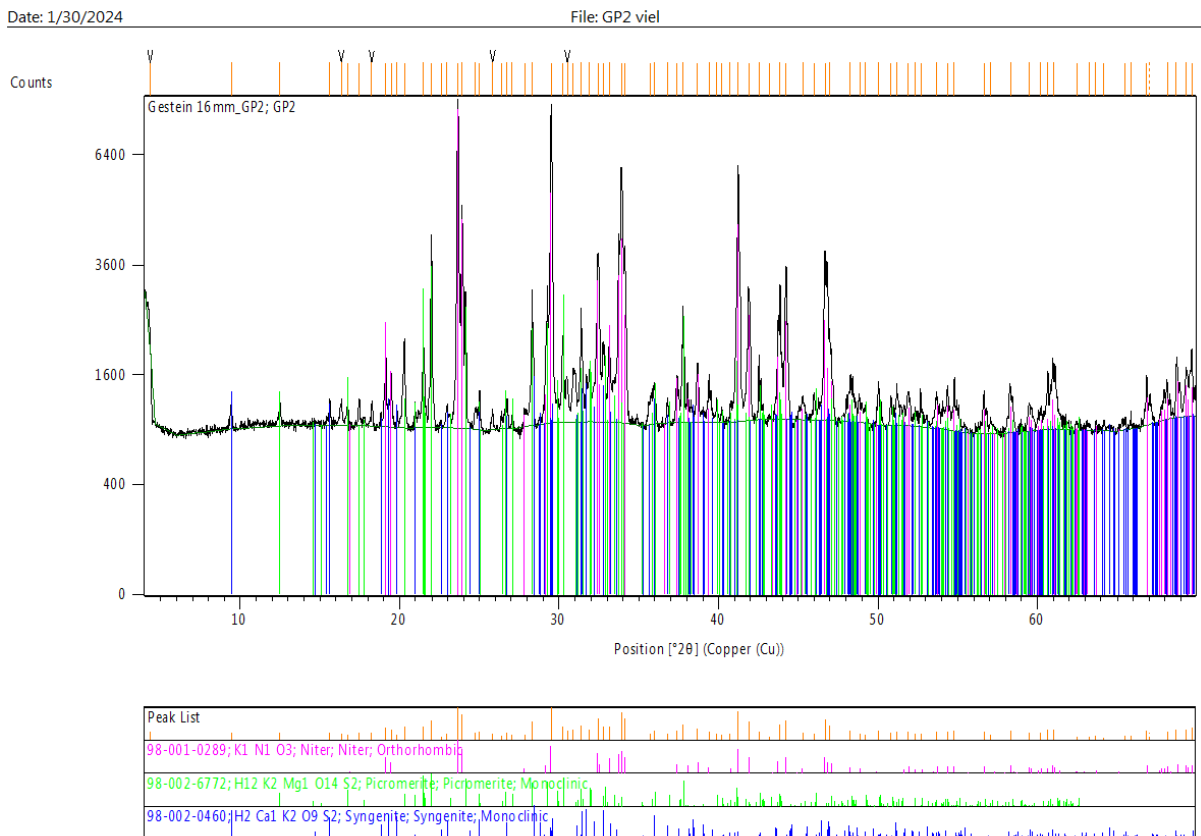
fig. 3: Sample 2, up to 1mm thick compact white crust (DF)

fig. 4: Sample 2, XRD spectrum

Sample 3.1 – Location: North arm, vault, East-wall E5

Description: thin crusts and fine-grained white salts, some particles are reddish (fig. 5).

Result by XRD: mostly dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$] and to a lower degree gypsum [$CaSO_4 \cdot 2H_2O$], maybe small amount of hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$] (fig. 6).

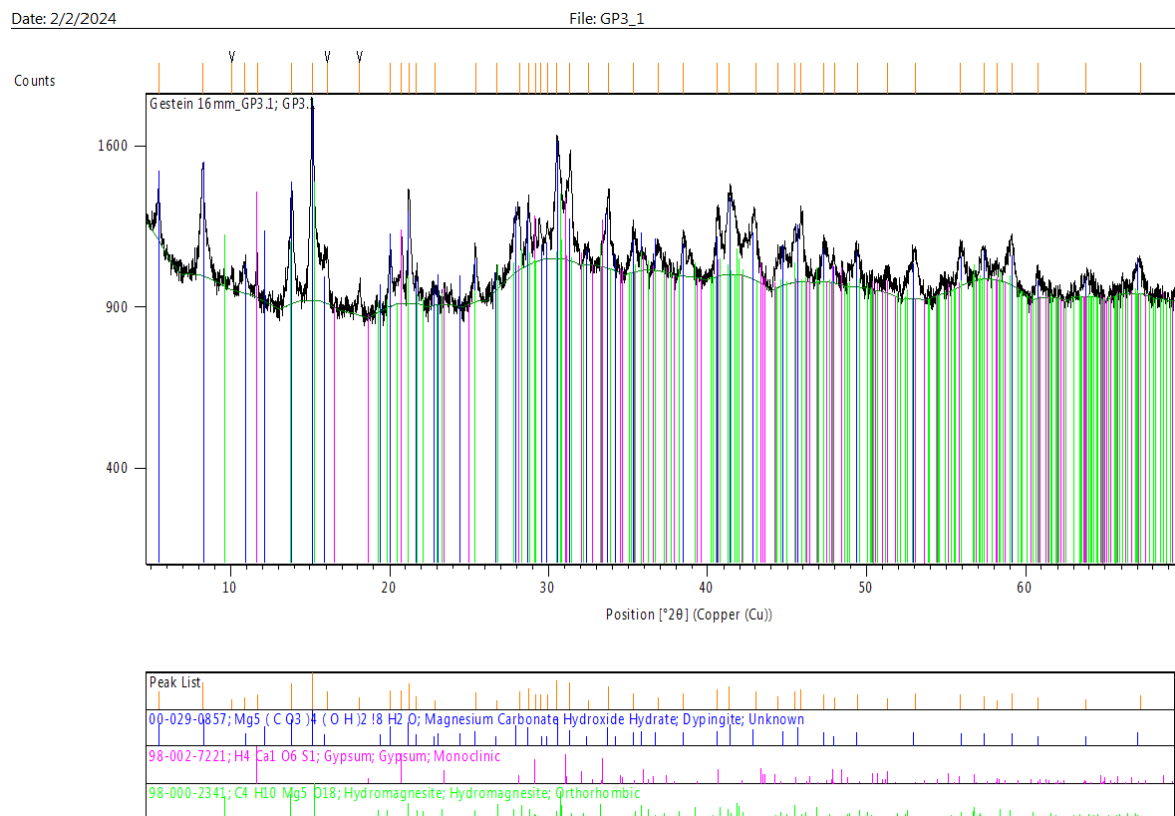fig. 5: Sample 3.1, thin white crusts with some reddish particles (DF)

fig. 6: Sample 3.1, XRD spectrum

Sample 3.2 – Location: North arm, vault, East-wall E5

Description: white small relative hard particles (parts of a crust?), some are yellowish (fig. 7).

Result by XRD: mostly dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$] and to a lower degree gypsum [$CaSO_4 \cdot 2H_2O$], maybe small amount of hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$] (fig. 8).
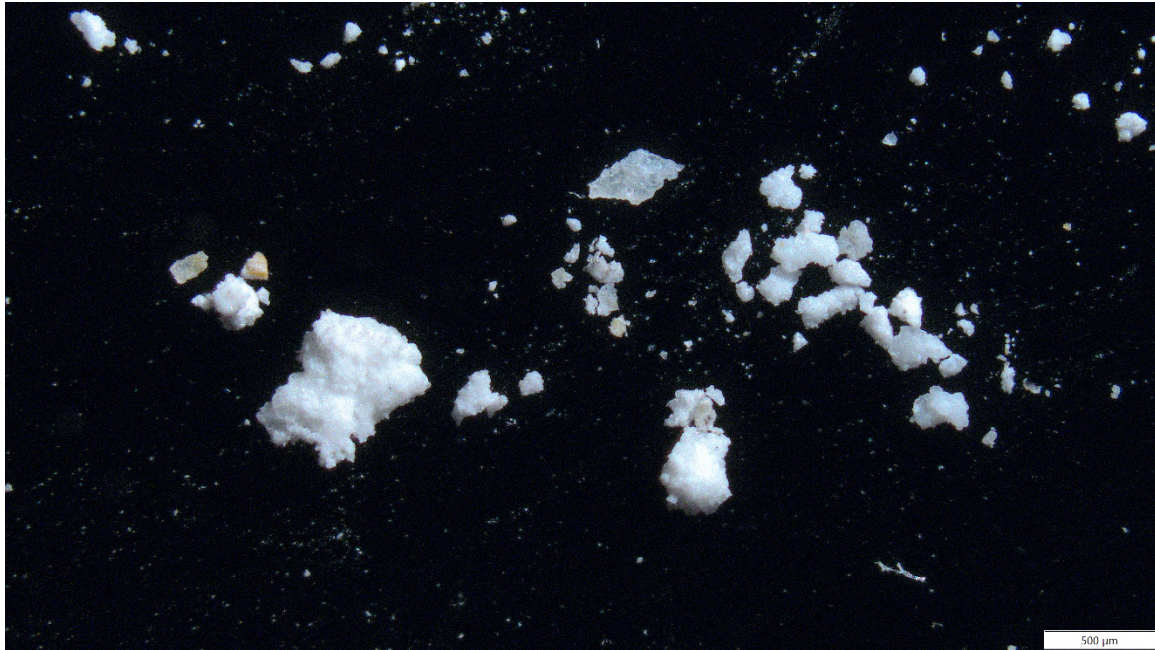

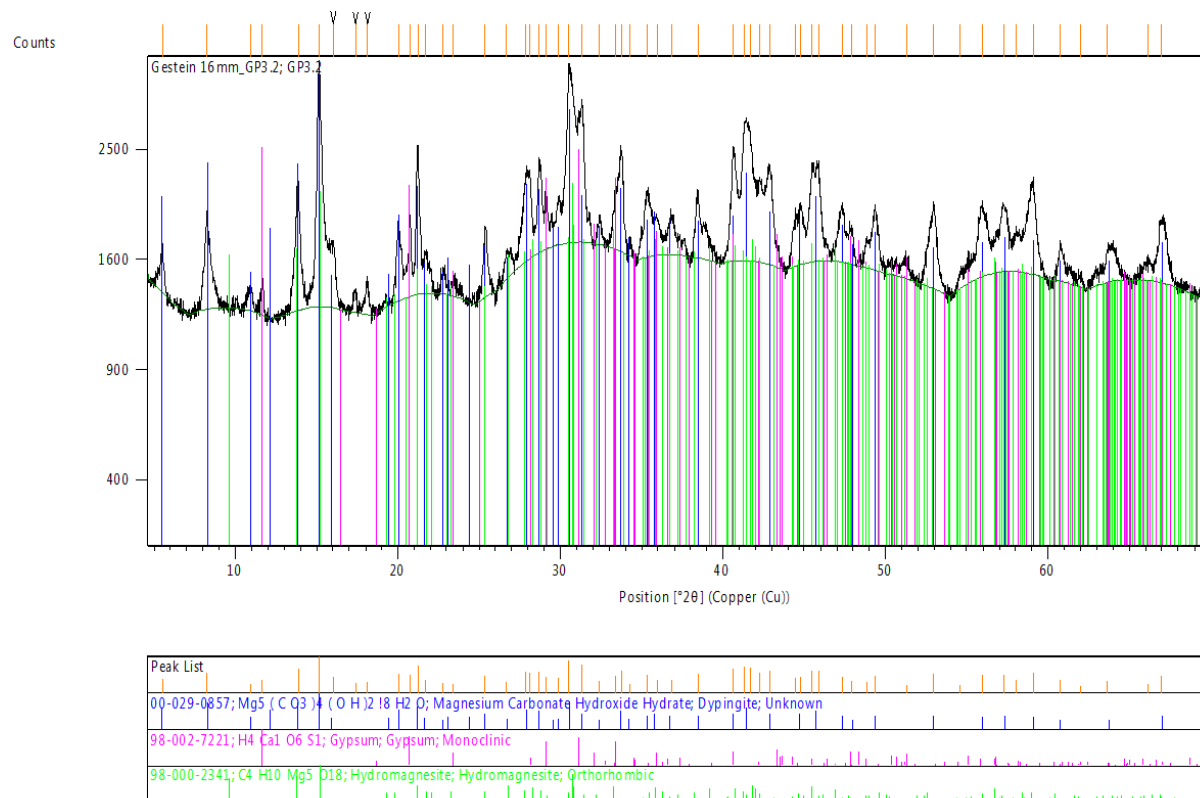fig. 7: Sample 3.2, white small relative hard particles (DF)

fig. 8: Sample 3.2, XRD spectrum, similar to sample 3.1

Sample 4 – Location: North arm, vault, East-wall E5

Description: white small fluffy particles, a few are reddish (fig. 9).

Result by XRD: mostly hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$], to a lower degree dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$] and maybe a small amount of niter [KNO_3] (fig. 10).
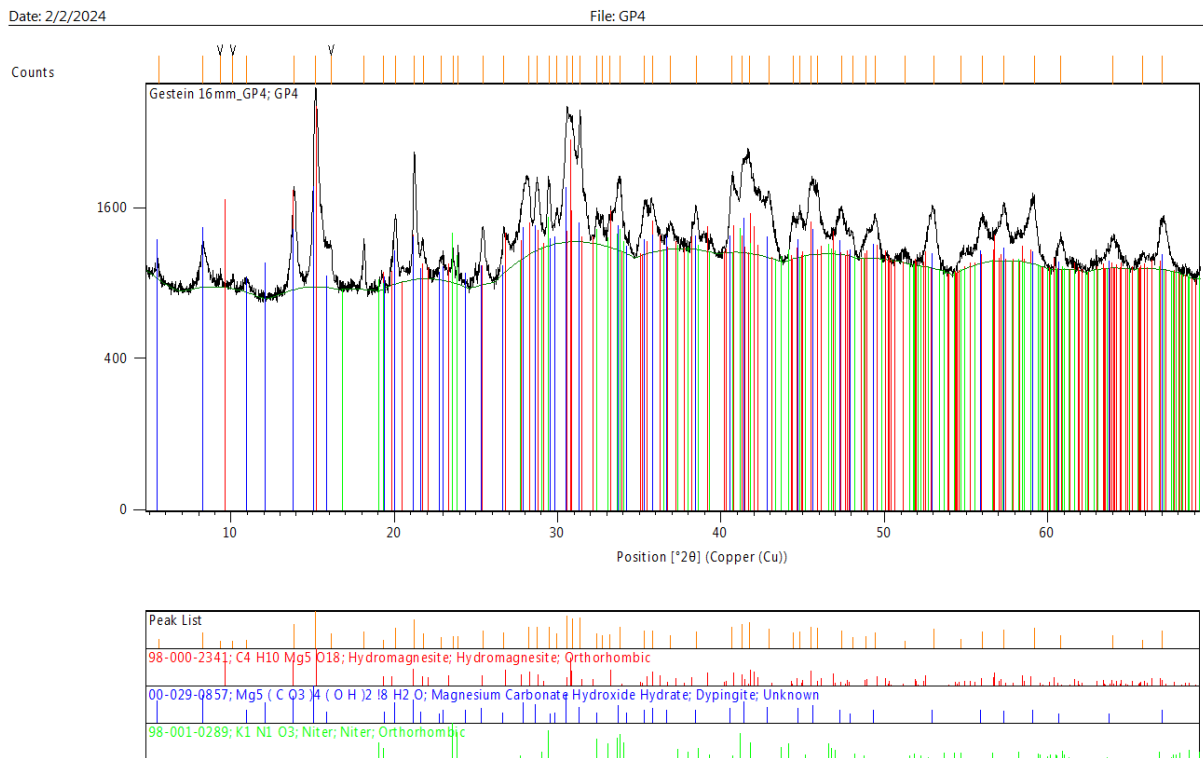

fig. 9: Sample 4, white small fluffy particles (DF)

fig. 10: Sample 4, XRD spectrum

Sample 5 – Location: Pendantive, 4

Description: mostly whisker and some granular crystals (fig. 11) – similar to sample 1
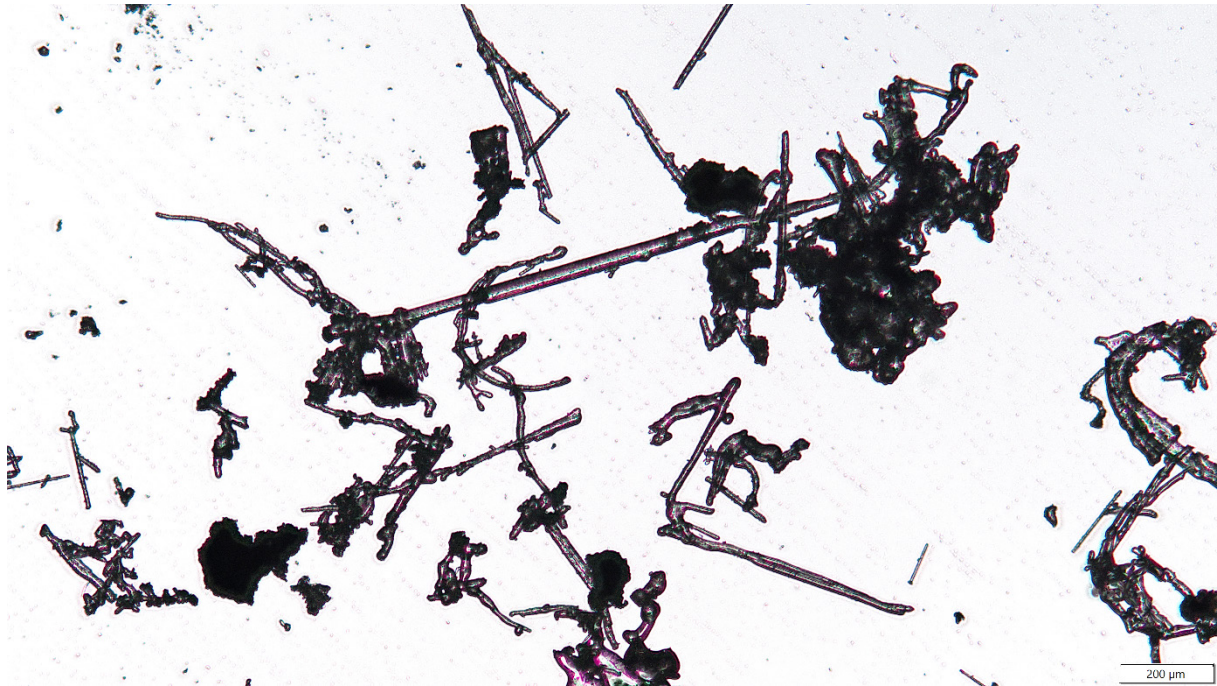
Result: niter [KNO_3] (fig.12).

fig. 11: Sample 5, mostly whisker and some granular crystals (II-pol oil) – similar to sample 1
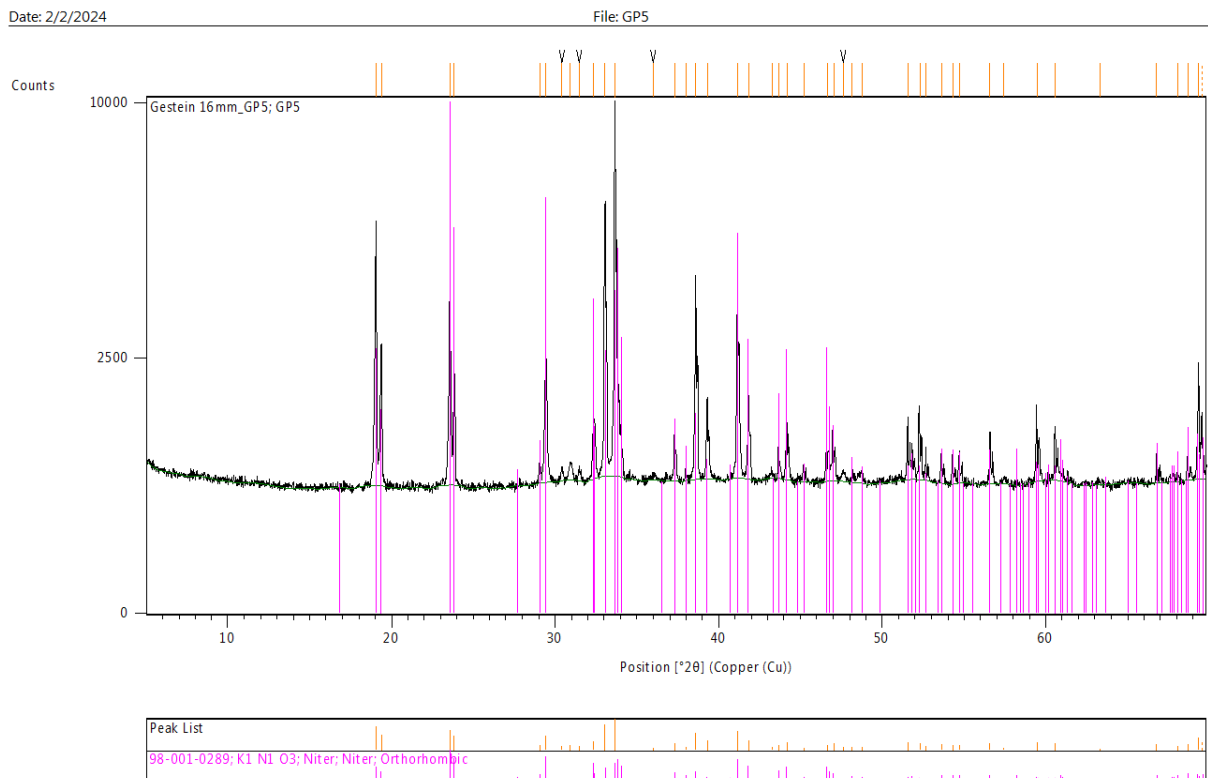

fig. 12: Sample 5, XRD spectrum

Sample 6 – Location: West arm, vault, C14

Description: white crust with blue paint layer particles (fig. 13).

Result by XRD: mostly nesquehonite [$MgCO_3 \cdot 3H_2O$], to a lower degree dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$] and maybe a small amount of hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$] (fig. 14).
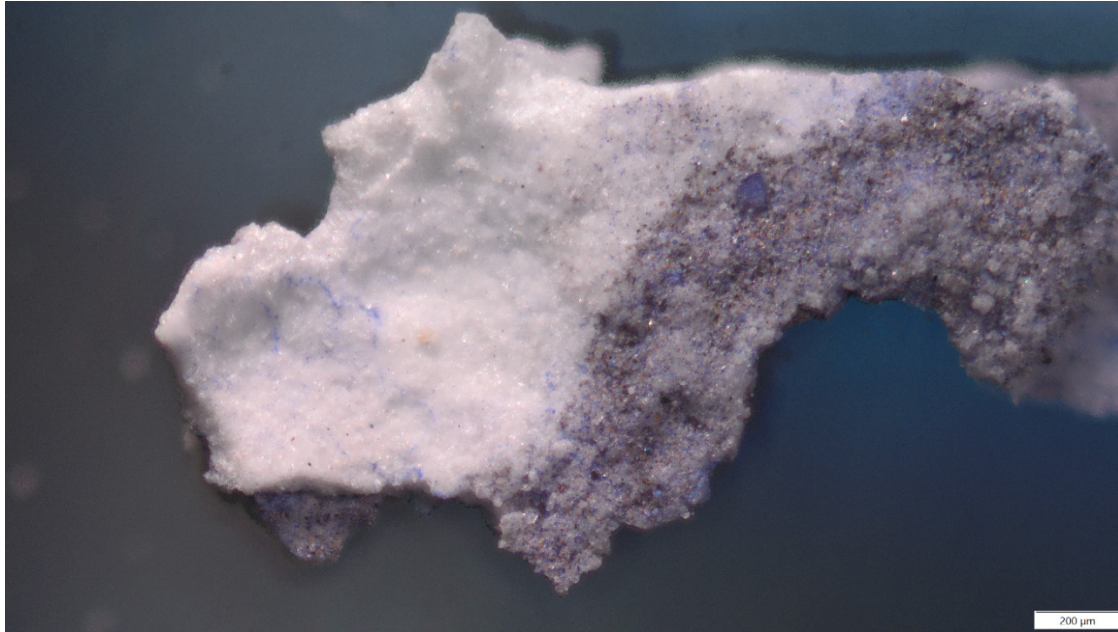

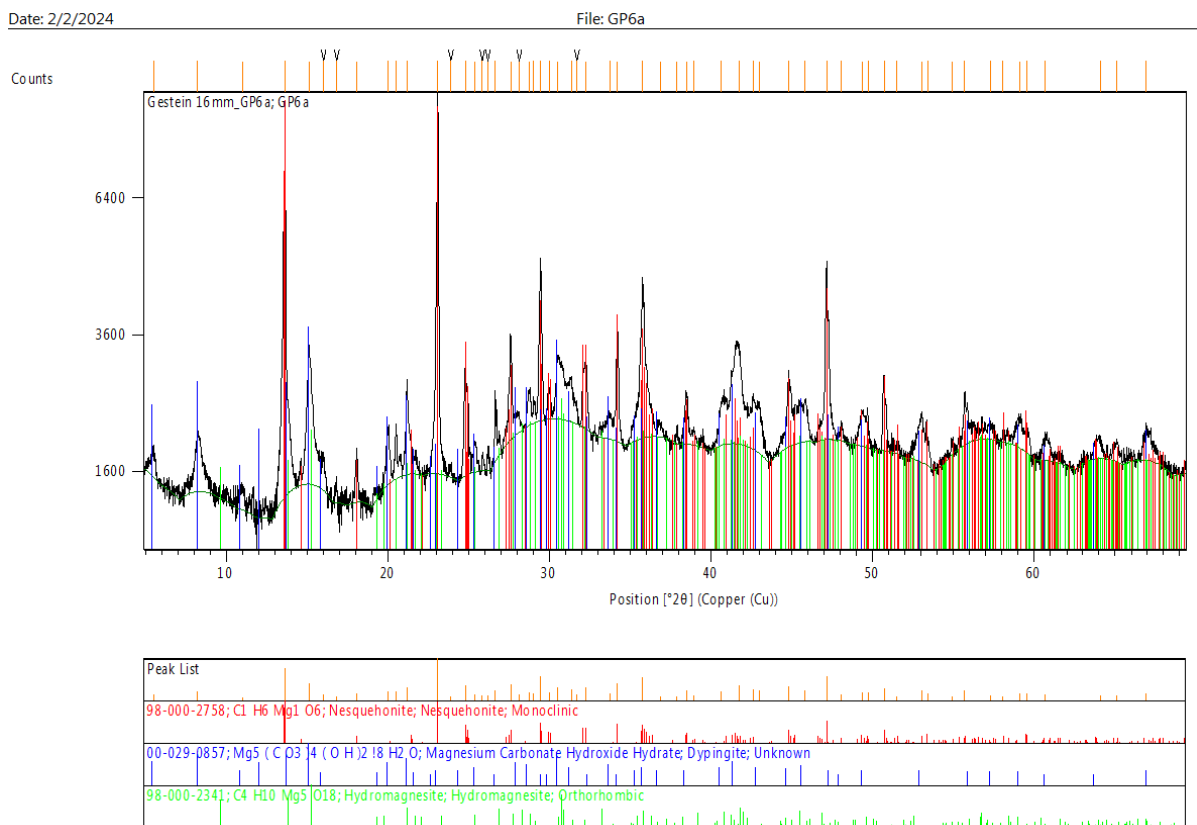fig. 13: Sample 6, white crust with blue paint layer particles (DF)

fig. 14: Sample 6, XRD spectrum

Sample 7 – Location: West arm, C14

Description: white, partly transparent crust with blue paint layer particles (fig. 15) – similar to sample 6.

Result by XRD: mostly nesquehonite [$MgCO_3 \cdot 3H_2O$], to a lower degree dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$] (fig. 16).
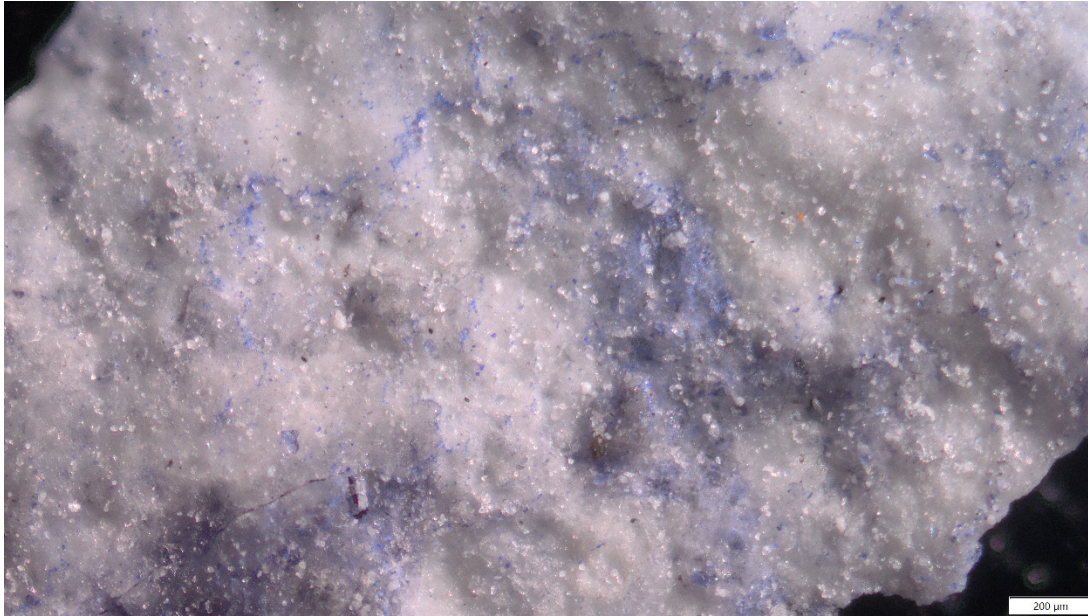

fig. 15: Sample 7, white, partly transparent crust with blue paint layer particles (DF)
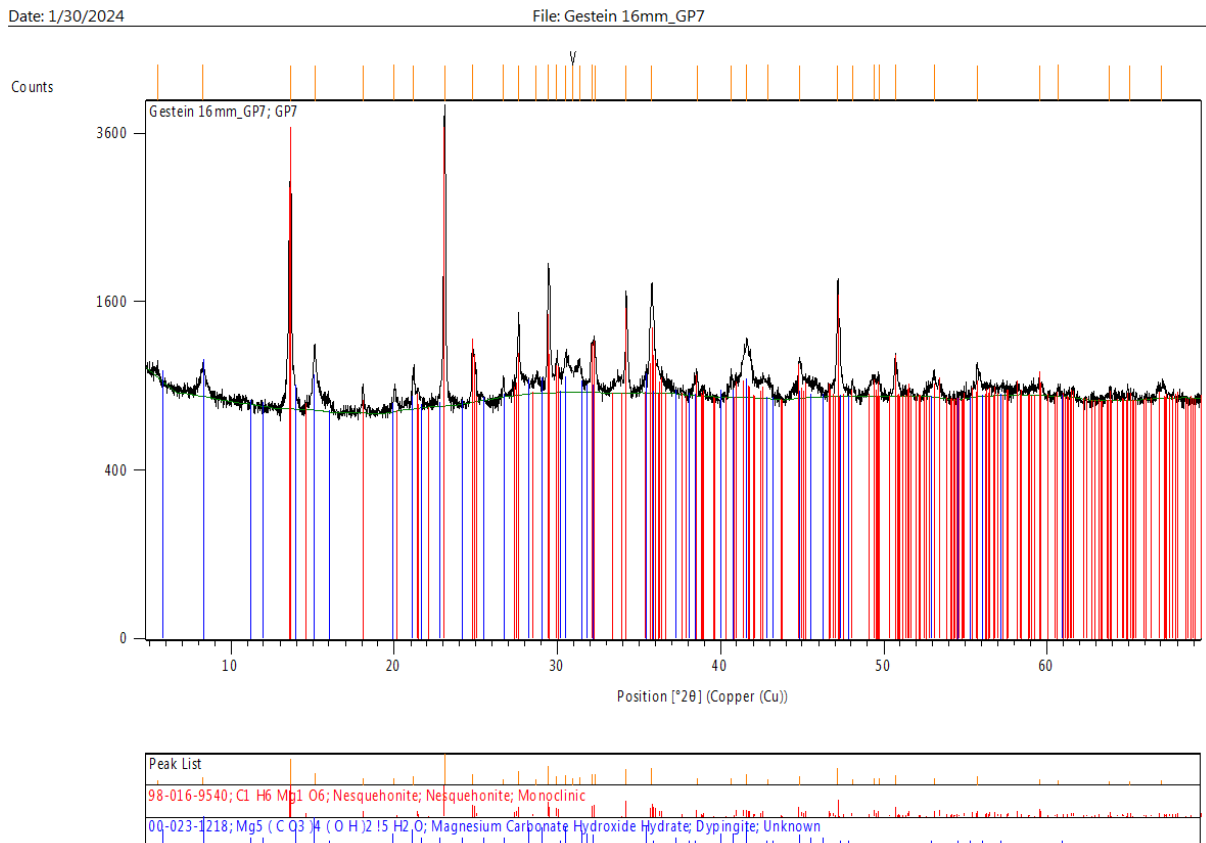

fig. 16: Sample 7, XRD spectrum

10

Sample 8 – Location: West arm, S8

Description: granular crystals (partly agglomerated to a crust) and whisker (fig. 17) – similar to sample 1 and 5.

Result: niter [KNO_3] (fig. 18), calcite [$CaCO_3$] probably derives from the plaster or paint layer.
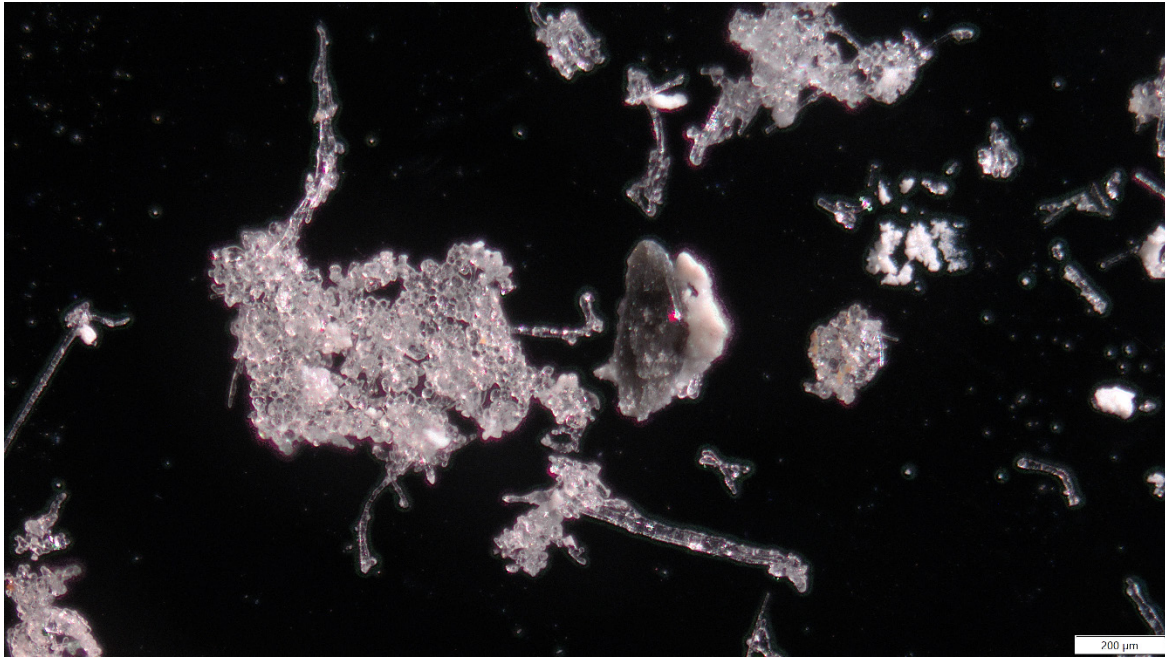

fig. 17: Sample 8, granular crystals and whisker (DF) – compare to sample 1 and 5
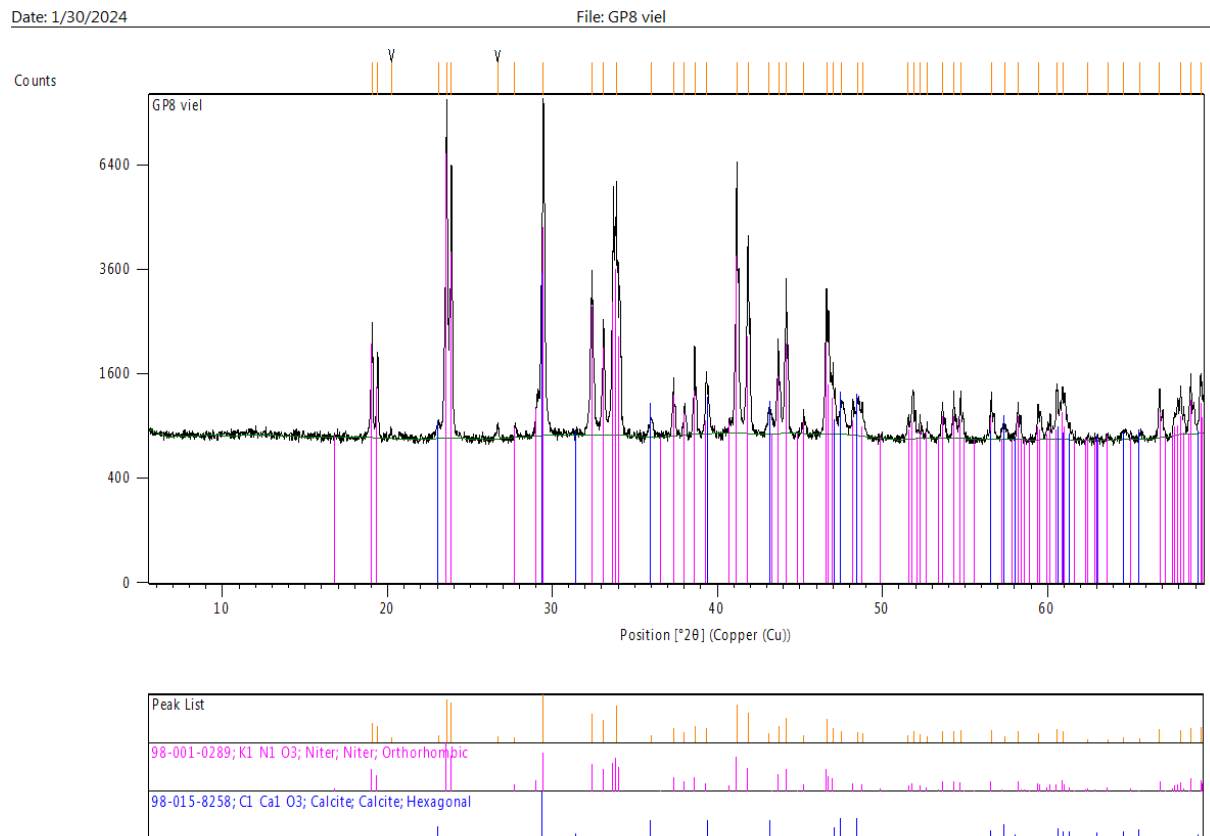

fig. 18: Sample 8, XRD spectrum

Sample 9 – Location: South arm, W5

Description: transparent granular and short columnar crystals (whisker) (DF) (fig. 19).

Result by XRD: mostly hexahydrite [$MgSO_4•6H_2O$] and to a much lower degree gypsum [$CaSO_4•2H_2O$] (fig. 20).
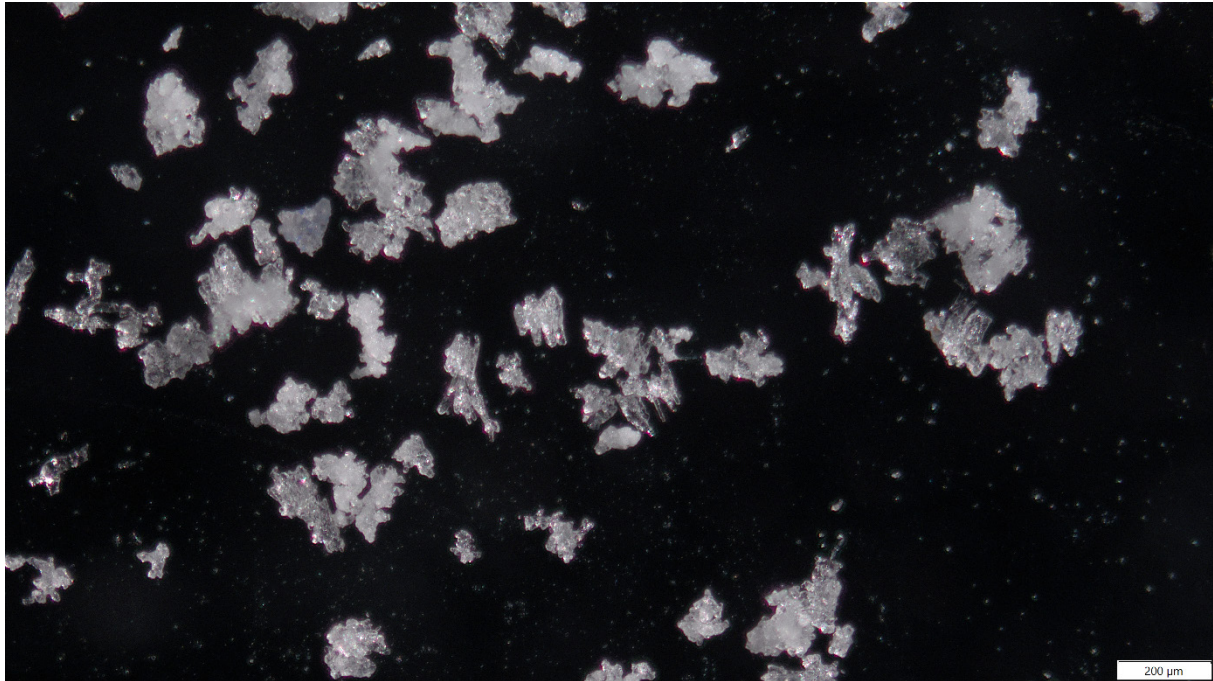

fig. 19: transparent granular and short columnar crystals (whisker)
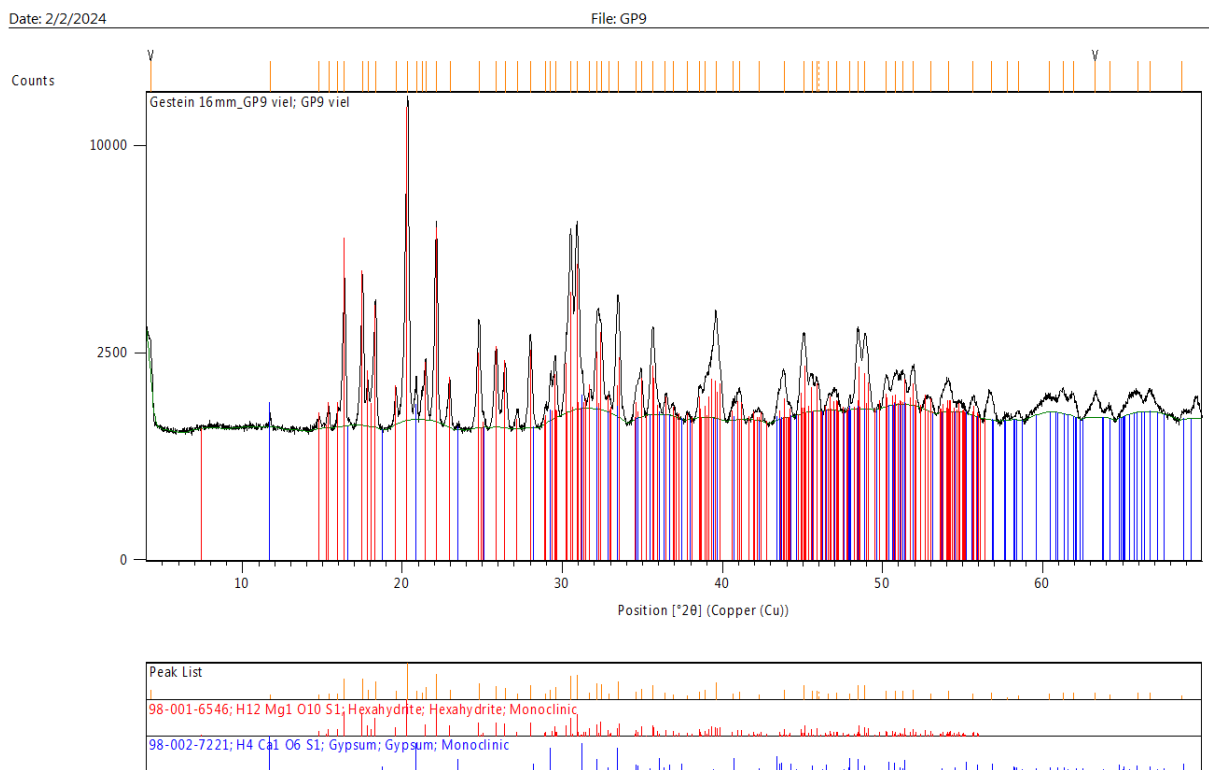

fig. 20: Sample 9, XRD spectrum

Sample 10 – Location: South arm, W5

Description: white crust with blue particles (fig. 21) – similar to sample 6 and 7.

Result by XRD: mostly nesquehonite [$MgCO_3 \cdot 3H_2O$], to a lower degree dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$] (fig.22).
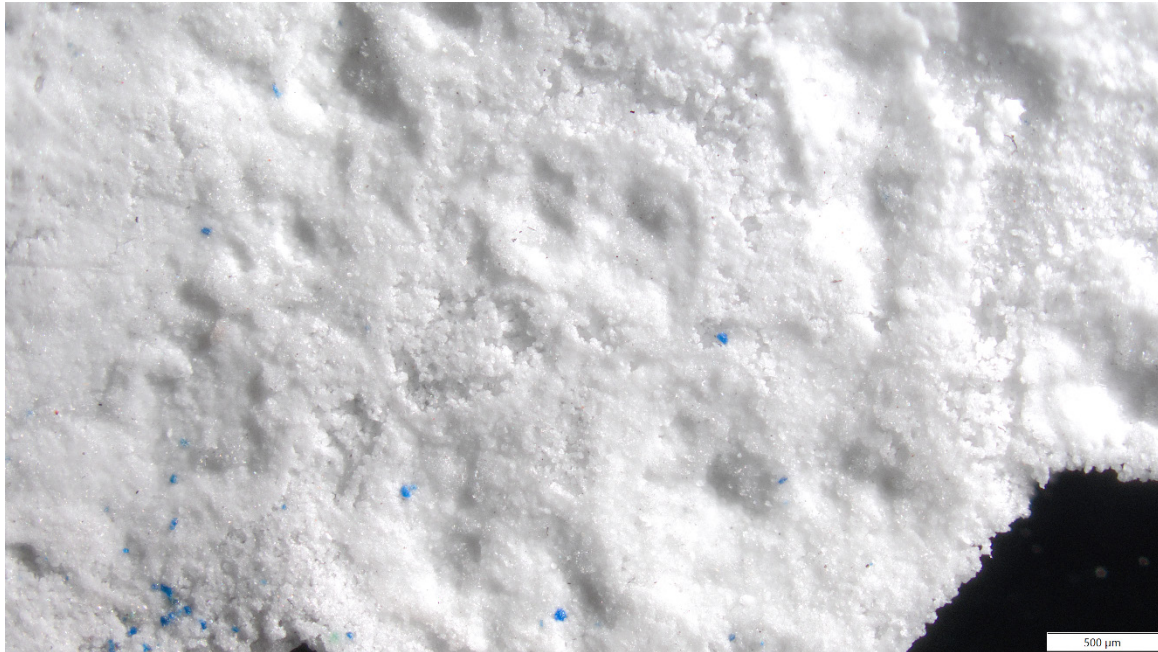

fig. 21: Sample 7, white, partly transparent crust with blue paint layer particles (DF)
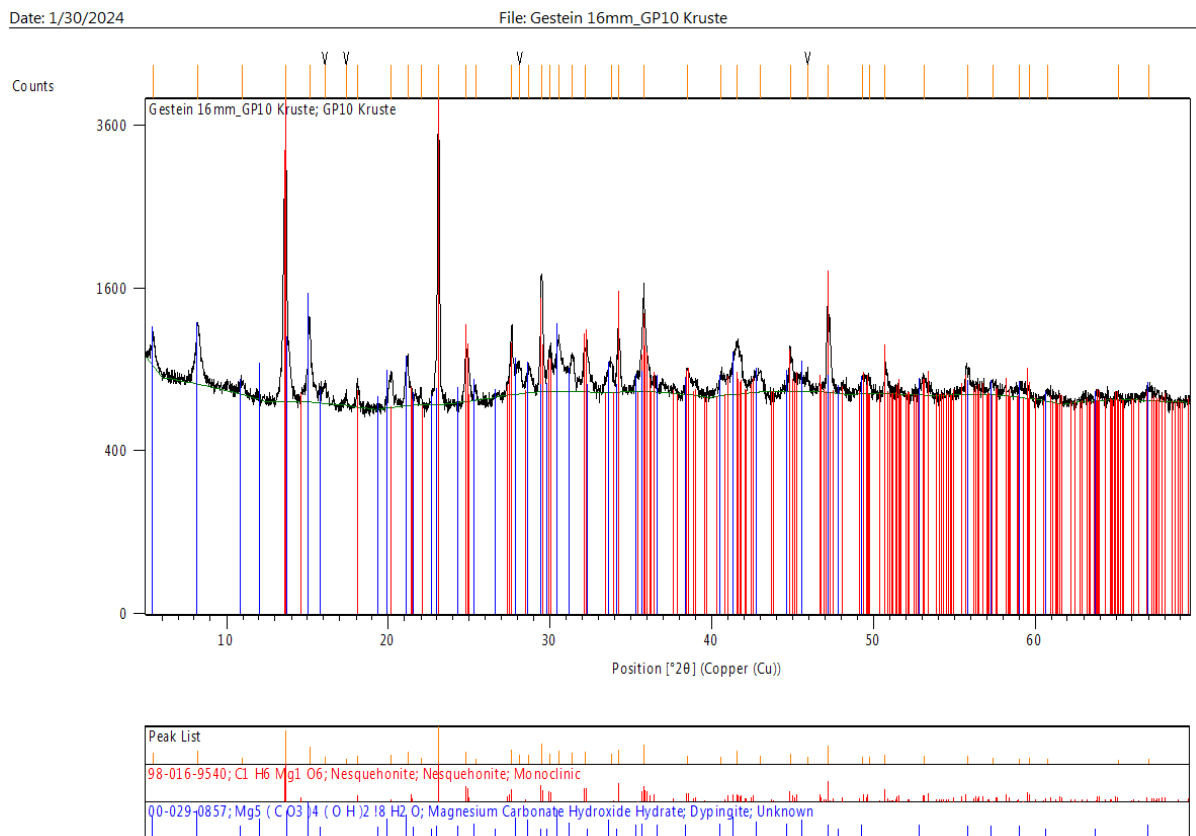

fig. 22: Sample 10, XRD spectrum

Summary and outlook

The results so far have shown that, in addition to some gypsum, at least three different salt systems in particular contribute to the damage:

1. Magnesium carbonate

2. Magnesium sulfate

3. Potassium nitrate

In some samples, double salts of two cations and sulfate could also be detected (aphtitalite, picromerite and syngenite), which indicates the complexity of the salt ion mixtures in at least some areas of the walls.

All salts have different behavior depending on the solubility properties, the respective deliquescence humidities and whether they can hydrate and dehydrate (for further useful information see www.saltwiki.net).

In addition to the qualitative analyzes carried out so far, quantitative salt analyzes on sample material from selected depth profiles would provide information about the salt concentrations even in deeper wall or vault areas.

To minimize further damage from salts, it is essential to prevent further water additions. With each new entry of moisture, salts are dissolved, salt ions are mobilized, and new salt crystals can be expected when the water evaporates (the walls dry).

The salt ion sources should be identified in additional studies. It may be possible to minimize additional potential for damage in the future by removing the salt ion sources.

And how do the salts now in the walls relate to the climate? Monitoring of the salts on selected reference areas in combination with climate measurements is suitable in order to understand the crystallization processes taking place for each salt system.

After knowledge of the salt ion sources, knowledge of the quantitative contamination with salts in the walls and vaults and an understanding of the crystallization processes taking place, it is then possible to plan suitable salt reduction measures and further conservation interventions.