The VOLATILE4ARCHAEO project: A technical report for conservators

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1. The VOLATILE4ARCHAEO project

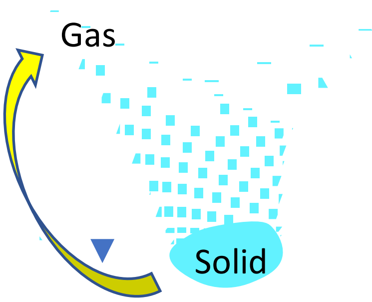
The project VOLATILE4ARCHAEO (Investigation of Volatile Binding Media in Temporary Consolidation of archaeological materials) was funded by the European Commission within the call H2020-MSCA-IF-2020 of the Marie Skłodowska-Curie Actions (Grant Agreement n. 101031224) (https://cordis.europa.eu/project/id/101031224).

Volatile binding media (VBM) are used to protect fragile heritage materials during transport or other high-risk operations. Cyclododecane (CDD) is currently the most used temporary consolidant. Still, this material exhibits some limitations, such as its possible toxicity for humans and the environment, its low flashpoint posing inflammation risks, and the fact that it provides a single sublimation rate, which makes it not suitable for all the climates and applications.

The EU-funded VOLATILE4ARCHAEO project investigated alternative VBM, alone and mixed with CDD. Sublimation rate, interaction and compatibility with various substrates, and presence of residues were tested. The project provided several options for variable-term consolidation with VBM and experimental data on their performance, including testing on real historical objects.

2. What are Volatile Binding Media (VBM)?

Volatile Binding Media waxy solids that sublime (pass directly from solid to gas phase) at room temperature, the major advantage of VBM is the ability to be removed, simply by evaporation, making the use of solvents and mechanical action obsolete.



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3. Current applications of VBM on historical materials

VBM can be used for different purposes:

- Consolidation of Fragile objects in situ and conservation laboratories
- Facing of deteriorated surfaces
- Desalination of water-sensitive painted objects, lifting fragile wood, handling ethnographic objects, etc.

4. Objectives of the project

The project VOLATILE4ARCHAEO had three objectives:

(1) significantly advancing the understanding of the physical-chemical behavior of subliming compounds when used as temporary consolidants for conservation on different substrates via collaboration with materials science experts in the University of Bologna;

(2) investigating new types of VBM for the temporary strengthening of mural paintings and ceramic materials;

(3) validating the most promising VBM for conserving actual historical artifacts.

In VOLATILE4ARCHAEO, some selected VBM and their mixtures were systematically investigated and compared. Besides cyclododecane (CDD), the following emerging consolidants will be tested: **cyclododecane**, **menthol**, **camphene**, **cyclododecanone** and **cyclododecanol**, and fifteen mixes prepared and tested.

5. The sublimating compounds and their mixes

In the project VOLATILE4ARCHAEO, investigation and comparison of five VBM and 15 mixtures were carried out. They were also applied on various substrates, including limestone, marble, glass slides, painted plaster, painted pottery, and painted mortar.

The pure VBM were:

- Cyclododecane, $C_{12}H_{24}$ (CDD). The melting temperature is 63°C
- Cyclododecanol, $C_{12}H_{24}O$ (CDNOL). The melting temperature is 76-79°C
- Cyclododecanone, $C_{12}H_{22}O$ (CDNONE). The melting temperature is 62°C
- Camphene, $C_{10}H_{16}$. The melting temperature is 48-52°C
- Menthol, $C_{10}H_{20}O$. The melting temperature is 32-36°C

and their formula and properties are reported in Table 1. The mixes are reported in Table 2 and Figure 1.

Some of the mixes were considered as more promising in terms of workability, as they resulted well mixable, homogeneous, not sticky, hence they were selected for further testing: M1, M3, M5, M7, M8, M11, M12 and M13.

Table 1. The pure VBM investigated according to the technical datasheets.

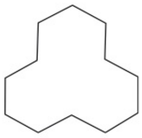
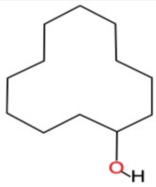
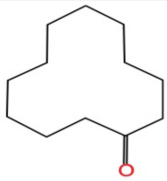
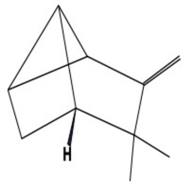
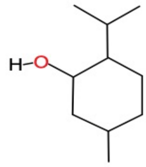
VBM **(Label)**	Cyclododecane (CDD)	Cyclododoecanol (CDNOL)	Cyclododecanone (CDNONE)	Camphene	Menthol
Structure					
Appearance	Crystal powder	Crystal	Crystal- powder	Crystal	Crystal
Color	White	White	White	White/colorless	White
Odor	-	-	-	Camphor-like	Mint like
Density (g/cm^3)	0.82	0.9	0.9	0.839	0.9131
Melting point	63°C	76-79 °C	62 °C	48-52°C	32-36 °C
Boiling point	111°C	272.7	113	159-160°C	216

Table 2. The mixes investigated.

Mix name	**Camphene**	**CDD**	**CDNOL**	**CDNONE**	**Menthol**
M1	-	50	50	-	-
M2	50	-	50	-	-
M3	25	-	75	-	-
M4	-	-	50	-	50
M5	-	-	75	-	25
M6	-	50	-	-	50
M7	-	75	-	-	25
M8	-	75	25	-	-
M9	50	-	-	50	-
M10	25	-	-	75	-
M11	-	-	25	75	-
M12	-	-	50	50	-
M13	-	50	-	50	-
M14	-	-	-	50	50
M15	-	-	-	75	25

Figure 1. The selected VBM and mixes utilized in the experimental work.

Table 3. Melting and crystallization temperatures found for the most promising mixes.

	M1	M3	M5	M7	M8	M11	M12	M13
$T_{melting}$ (°C)	62	67; 80	60	55	63	59	59	59
$T_{cryst.}$ (°C)	58	58; 76	53	50	57	55	55	52

6. VBM application techniques

Different application techniques were investigated, as described in the following.

a) Batik wax painting tool (Figure 2)

The tool has an electrical heater for melting the wax in the pan and a nozzle to cast the liquid wax.

Advantages:

- It is possible to control the required amount of VBM and rate per time
- It preserves the temperature, keeping the VBM liquid during the application time
- By using a stopper, it is possible to control the sublimation for the protection of humans and the environment.

Disadvantages:

- It can be used only for small samples, but it could be developed by using different shapes and sizes of nozzle or adding a source of pressure
- It is easy to use for horizontal artifacts and vice versa for vertical artifacts.

b) Brushing (Figure 3)

Advantages:

- It is appropriate for vertical and horizontal artifacts
- It can be found in different sizes

Disadvantages:

- It is suitable only for surfaces and artifacts in good condition, as it touches the artifact surface and may cause a fall or move of surface fragments
- It may lead to losing part of the VBM and less control
- It causes sublimation to the environment and humans in the application site
- It requires changing the brush from time to time.
- The VBM solidifies, which may require another melting or heating because of the quick solidification.

Figure 2. The batik wax painting tool.

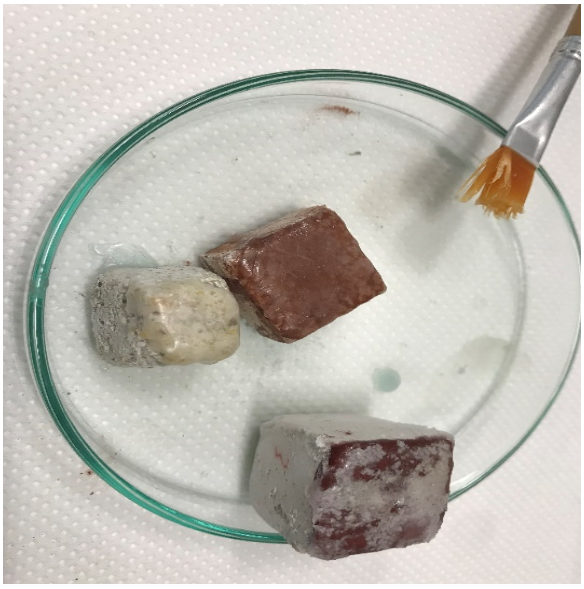


Figure 3. The brushing of the VBM.

c) Pouring (Figure 4)

This technique is used mainly in excavation sites.
Advantages:

- It is applicable especially where no facilities are present.

Disadvantages:

- It involves a minimum control
- It may cause wasting of VBM
- It does not prevent sublimation to the environment and humans
- It may lead to different thicknesses, and this prevents the prediction of the sublimation rate.

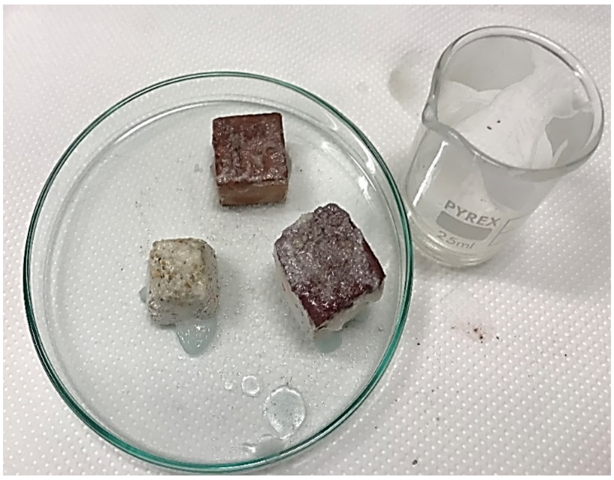


Figure 4. Pouring of the melted VBM.

The batik wax melter was used to apply the VBM in this study to obtain more controlled and uniform distribution of the melted materials.

7. Microscopic investigation of the VBM over different substrates

The aspect and adhesion of the materials poured in the melted state over different substrates were investigated by a stereo-optical microscope and some examples are reported in Figure 5. The stereo-microscope was used to: a) characterize the volatile binding media and mixes, b) observe the behavior of VBM and mixes on the substrates, and c) detect the residue presence on the substrates after sublimation. The microscopic examination showed a similar appearance of CDD and CDNONE (waxy, shiny). However, CDNONE is whitish than CDD. The menthol's crystalline shape shows the gradual growth of crystals during cooling. No residue was detected using the microscope, which led to alternative techniques, including FTIR, SEM, and fluorescent microscope.

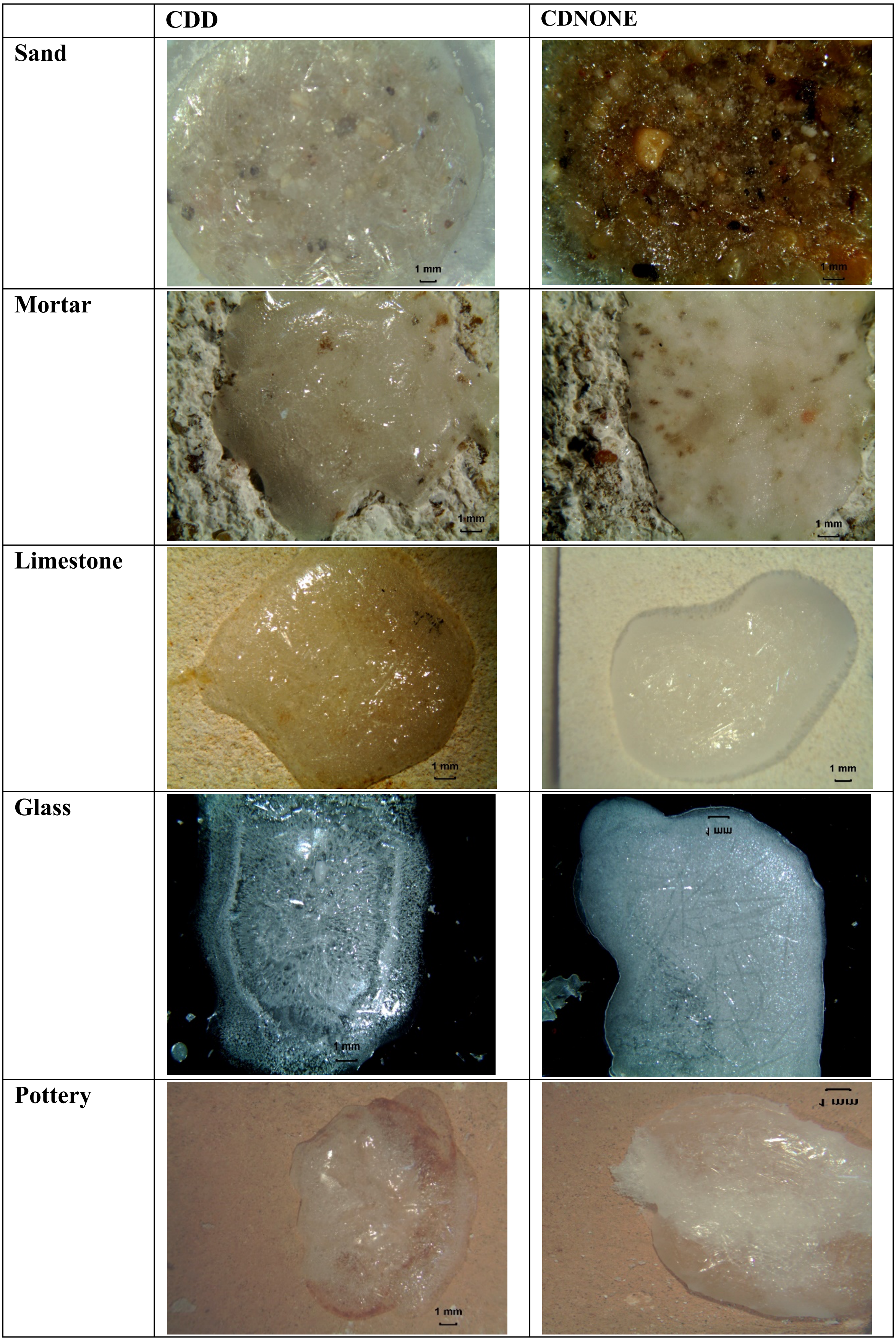


Figure 5. A stereo-optical microscope observed examples of the VBM over different substrates.

8. Sublimation rate

The sublimation rate of the volatile binding media is one of the most critical factors for conservators. Here, selected VBM were poured over different materials and their weight loss over time was monitored under exposure to two different temperatures (20°C and 30°C).

Figures 6-11 show the weight loss of selected volatile binding media on marble (Carrara marble), limestone (porous bioclastic Lecce stone), and glass slides over the first 1000 hours.

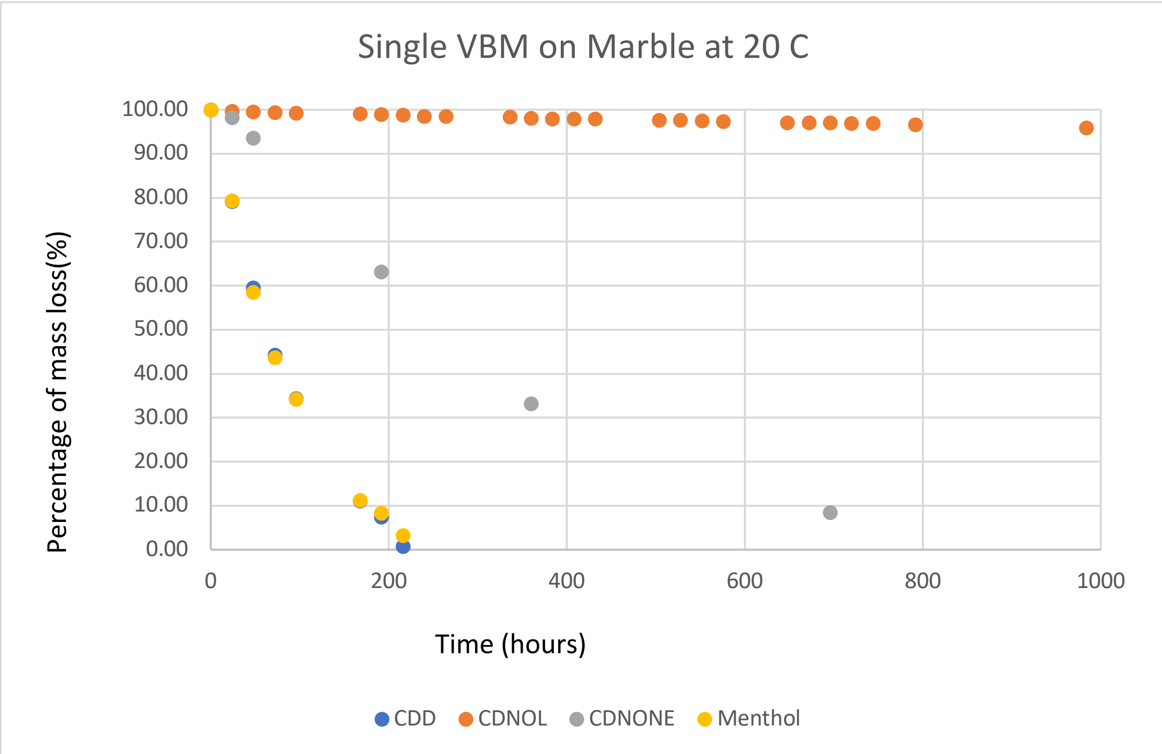


Figure 6. Sublimation rates of single VBM applied on marble, at 20°C

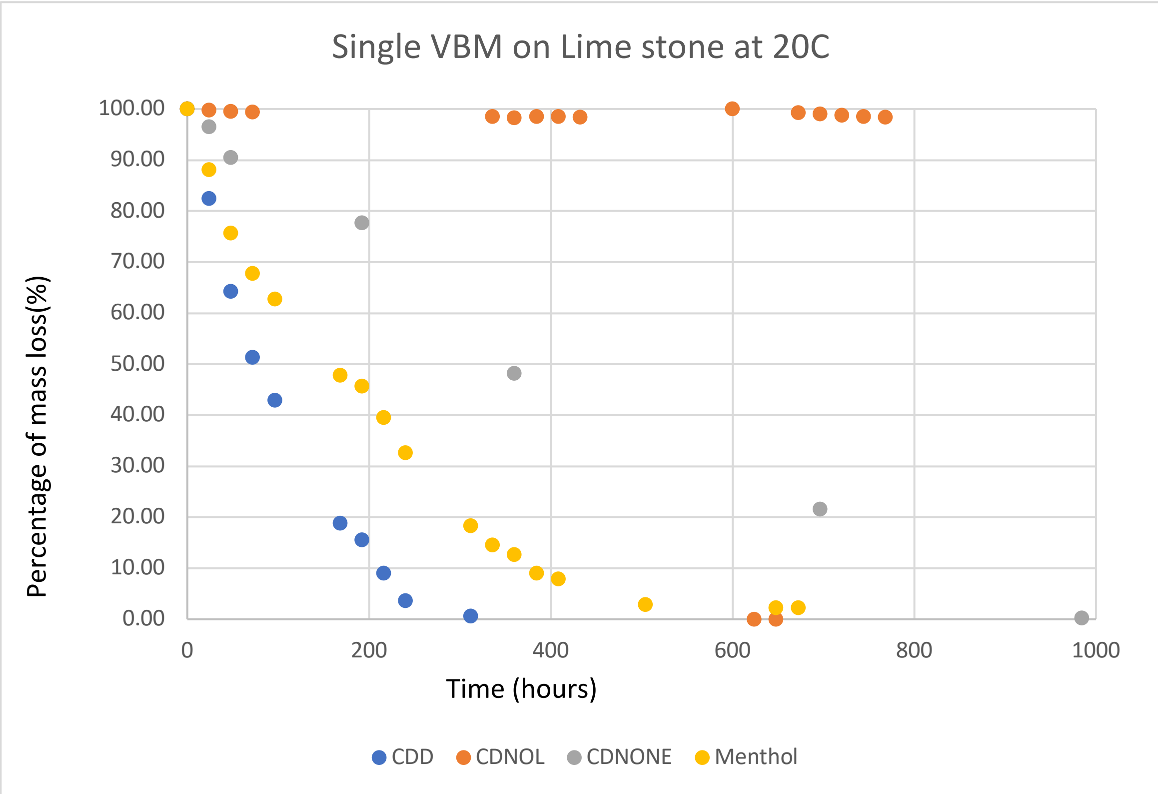


Figure 7. Sublimation rates of single VBM applied on limestone, at 20°C

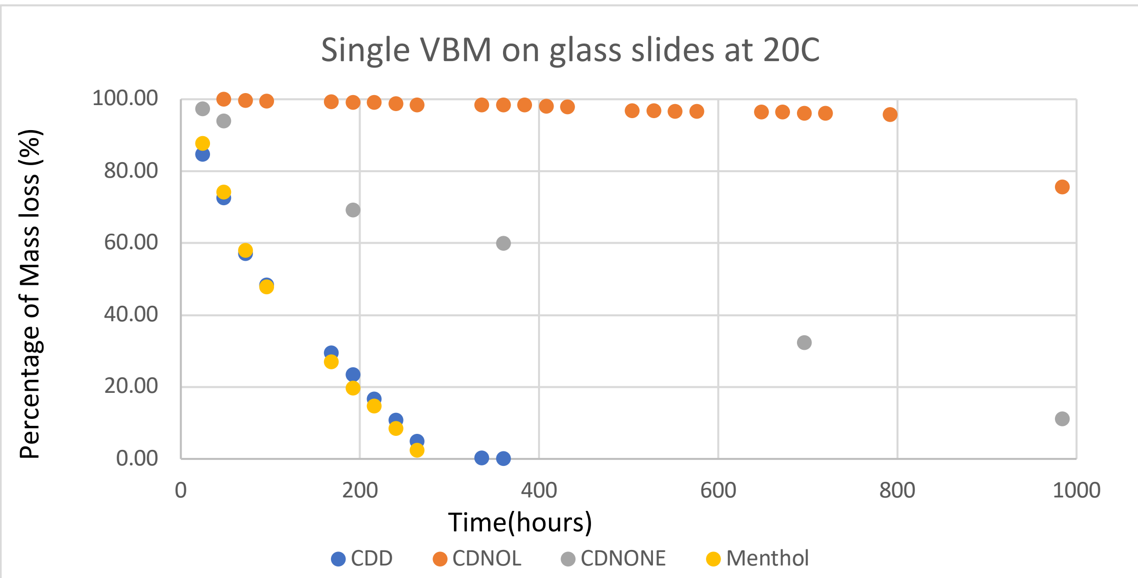


Figure 8. Sublimation rates of single VBM applied on glass slides at 20°C

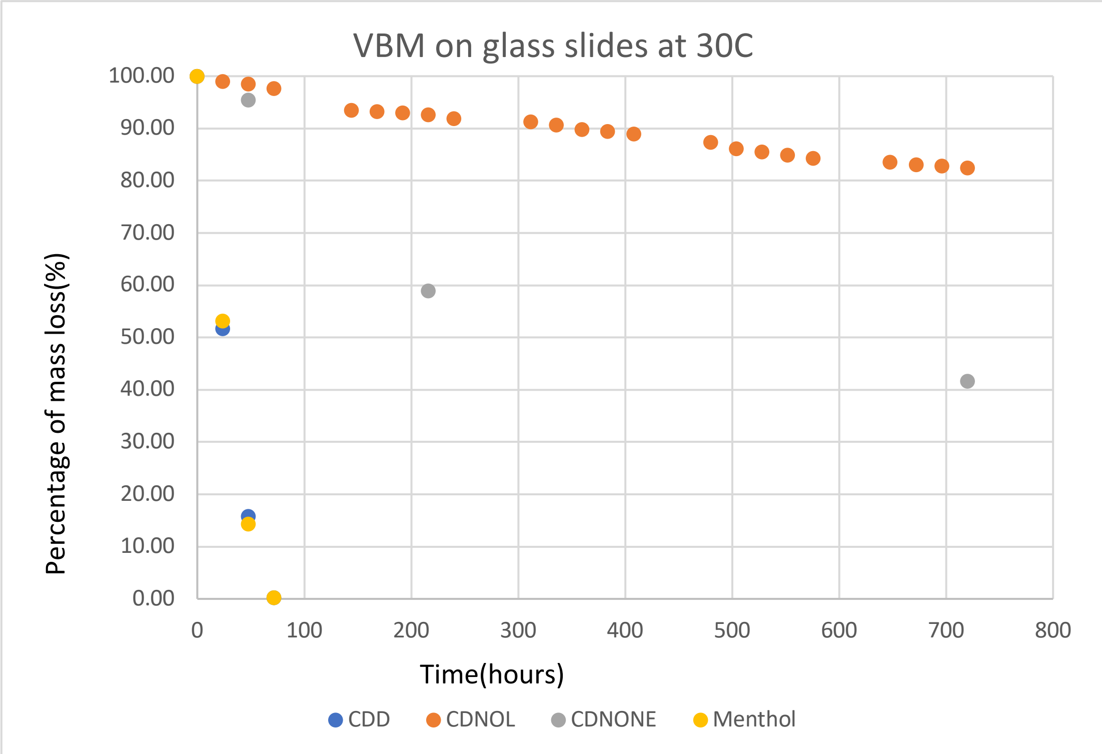


Figure 9. Sublimation rates of single VBM applied on glass slides at 30°C

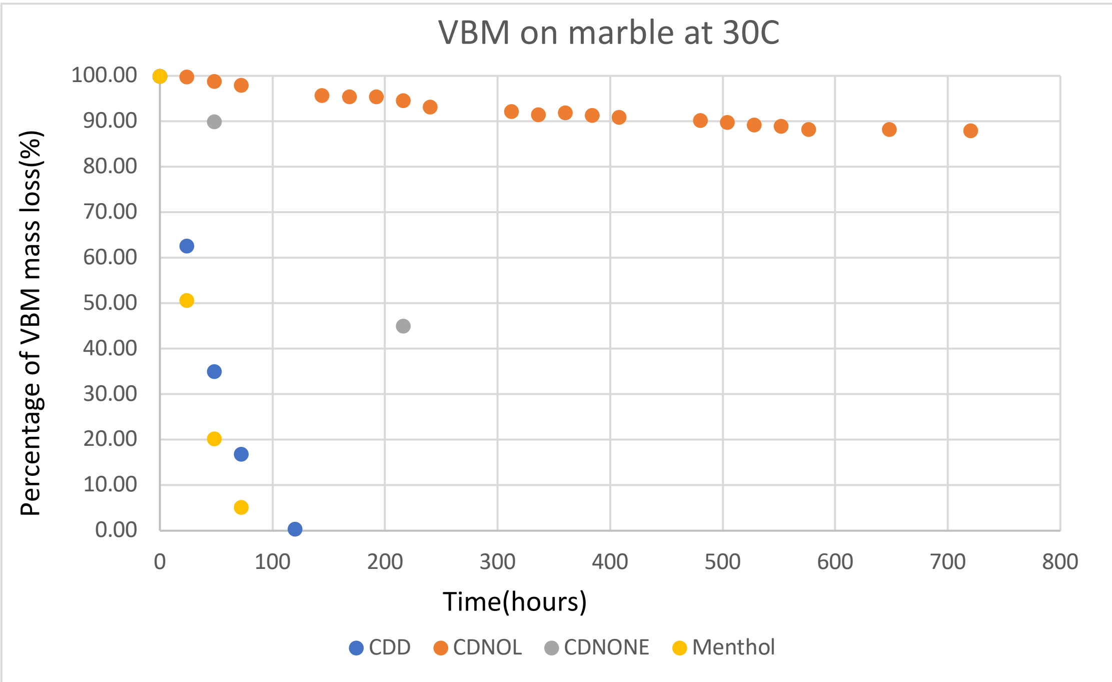


Figure 10. Sublimation rates of single VBM applied on marble at 30°C

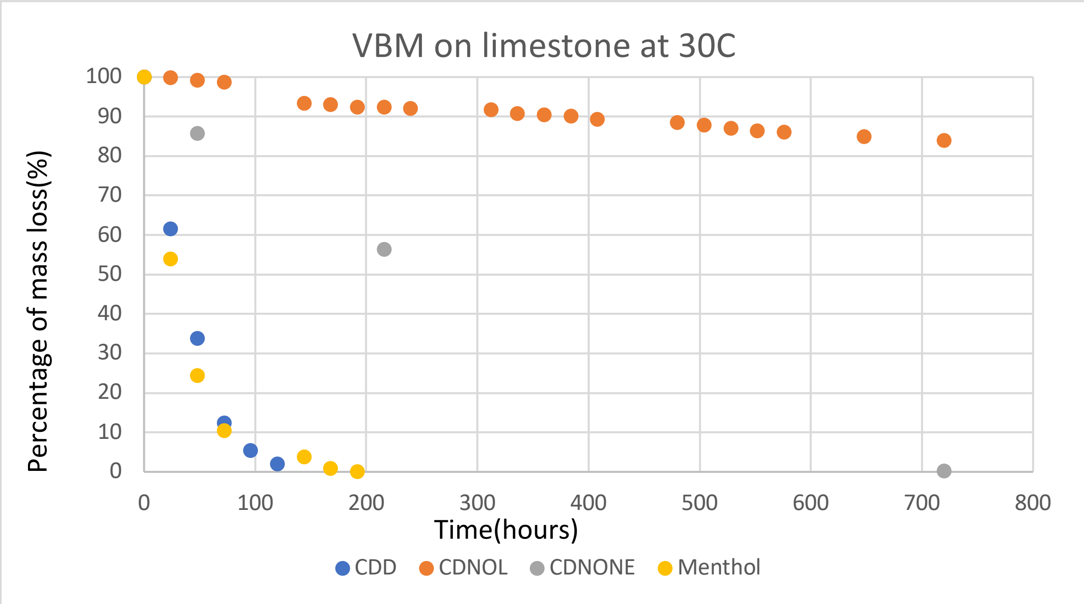


Figure 11. Sublimation rates of single VBM applied on limestone at 30°C

We can observe that:

- the sublimation speed at 30°C is much higher than at 20°C, indicating that the climatic conditions play a key role in the sublimation behavior of the VBM
- camphene is completely lost in about one day over all the substrates, hence it is considered suitable only for extremely short operations, which however are not so common in the conservation field. It is not reported in the figures.
- menthol is quicker than CDD, although in the same order of magnitude, hence they seem suitable for short-time operations and/or cold climates
- CDNOL is extremely slow, hence it seems suitable for very hot climates where CDD is too fast and/or long-term consolidation
- CDONONE is slower than CDD, but much faster than CDNOL, hence it represents a promising alternative for temporary consolidation
- when applied over a porous substrate, the VBM exhibits a certain slowing of the sublimation, likely due to some penetration in the pores
- it was not possible to make conclusive remarks on the role of surface chemistry (calcite in the case of marble and silica in the case of glass).

Moreover, some mixes appear very promising too, as they allow to obtain a variety of sublimation speed:

- M7, mixture of CDD and menthol, which provides the fastest sublimation speed
- M8, mixture of CDNOL and CDD, which provides slow sublimation speed

- M11 and M12, mixtures of CDNOL and CDNONE, which provide and homogeneous and intermediate sublimation speed between the pure VBM
- M13, a mixture of CDD and CDNONE, provides slow sublimation compared to CDD and CDNONE.

Besides the data shown in Figures 6-11, **several factors were found to affect the sublimation rate:**

- Porosity of the substrate
- Chemical composition of the substrate
- Temperature
- Relative humidity (high relative humidity slows down the sublimation)
- Ventilation (air change)
- State of application (melt, spray, solution)
- Thickness of the VBM layer.

9. Presence of residues after sublimation

The presence of residues after sublimation of the VBM is a very important aspect, as it is strongly related to the reversibility of these materials and might affect the further possibility of treating the substrates.

This aspect was investigated by optical microscope, which highlighted no residues, and then by Fourier Transform Infrared Spectroscopy (FT-IR), which detected no bands ascribed to materials different from the substrates. However, when observed by fluorescent microscope, some small residues were found for all the materials investigated, including cyclododecane (Figure 12), for which no remains on the substrates have been highlighted before. These residues were confirmed by scanning electron microscopy (SEM) and microanalysis EDS.

Whether these residues may interfere with subsequent conservation treatments is hard to say, given the extremely small size and limited amount of these residues, and this aspect will be investigated in the future.

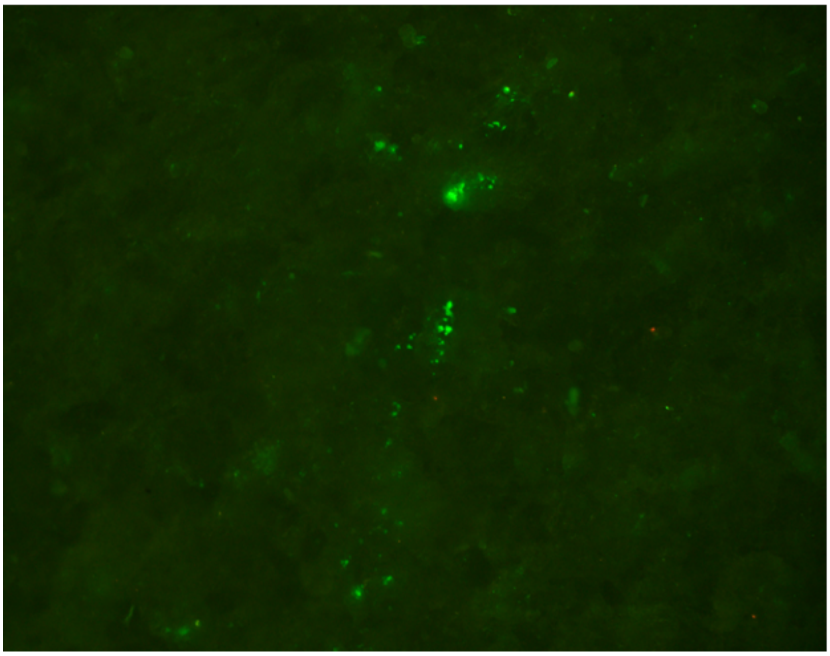


Figure 12. An example of residues from CDD found by fluorescent microscope.

10. Interactions with pigments

Interactions between VBM and pigments are of great interest in case of temporary consolidation of historic artifacts and mural paintings, hence they were specifically investigated at CICRP under the supervision of Dr. Jean-Marc Vallet. The following pigments were selected for testing: red hematite, Blue Ultramarine, Green Earth and Black carbon. The pigments were mixed with the VBM and mixes (Figure 13) and FT-IR investigated the possible occurrence of chemical reactions. Moreover, the samples were observed by optical microscope to highlight any change in the morphology.

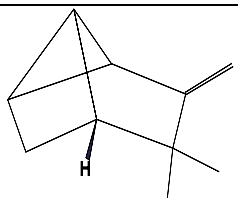
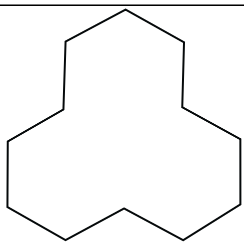
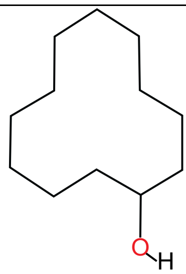
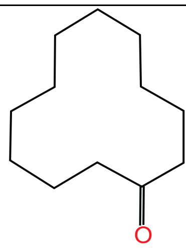
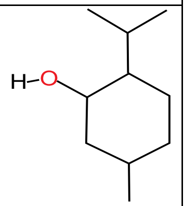
Figure 13. Mixes of the VBM consolidants with the pigments and consolidants alone for comparison.

The results highlighted that no chemical interaction occurred between VBM and pigments, and the solidified VBM's crystal size was unaffected by the pigments.

11. VBM-related hazards

Knowledge of the hazards related to the investigated VBM is paramount in view of their possible application. Table 4 summarizes the VBM properties, and the possible hazards for humans and the environment, and the corresponding protection measures according to the currently available information.

Table 4. The VBM-related hazards in the project VOLATILE4ARCHAEO.

	Camphene $C_{10}H_{16}$	Cyclododecane (CDD), $C_{12}H_{24}$	Cyclododecanol $C_{12}H_{24}O$	Cyclododecanone $C_{12}H_{22}O$	Menthol $C_{10}H_{20}O$
CAS no. and Supplier	CAS: 79-92-5 Merck	CAS:294-62-2 TCI	CAS:1724-39-6 AlfaAesar	CAS: 830-13-7 TCI	CAS: 89-78-1 ACROS ORGANICS ThermoFisher
Structure					
Properties	Colorless to white crystals Molecular weight **MW**: 136.23g/mol Melting 48-52°C	White crystal **MW** 168.32 g/mol Melting 63°C	Solid white crystal **MW** 184.32 g/mol Melting 76°C	Solid crystal powder **MW** 182.31 g/mol Melting 62°C	Solid white **MW** 156 .27 g/mol Melting 32-36°C
Human Health Health risks	Cause eye irritation Flammable LD50 Dermal> 2.500 mg/kg	Not a hazardous substance or mixture according to Regulation (EC) No 1272/2008 Acute Toxicity: LD50:>10 g/kg	This product doesn't contain any hazardous materials LD50 oral, LD50 > 2500 mg/kg	No data available about the effects	It is hazardous Skin and eye irritation May cause respiratory irritation LD50 = 3180 mg/kg

	Precautions	If injured consult Physician Ensure adequate ventilation Keep away from open flames. Give fresh air Wash skin with water and soap Wear Personal Protective Equipment **PPE**	Give fresh air or artificial respiration Skin: wash with soap and water Eye: wash Wear PPE	Ensure adequate ventilation Give fresh air or artificial respiration Skin: wash with soap and water Eye: wash Wear PPE	Ensure adequate ventilation Give fresh air or artificial respiration Skin: wash with soap and water Eye: wash Wear PPE	Ensure adequate ventilation Give fresh air or artificial respiration Skin: wash with soap and water Eye: wash Wear PPE
	Environmental hazards	Short-term acute aquatic hazard Long-term chronic aquatic hazard	Aquatic Hazard (Long-Term) Chronic Aquatic Toxicity May cause long-lasting harmful effects to aquatic life	May form combustible dust concentrations in air Aquatic hazard (long-term)	Aquatic hazard (acute) Aquatic hazard (long-term)	Combustible material.
	Environment protection	Avoid release to the environment. Carefully collect remainder as a hazard waste. Sweep into covered containers. Container tight closed. Don't recycle empty containers.	Store in a well-ventilated place. Disposal in specific containers. Avoid recycling empty containers.	Store in a well-ventilated place. Container well-sealed. Carefully collect remainder, as hazardous waste. Disposal in specific containers.	Avoid release to the environment. Carefully dispose of the remainder and containers in specific containers	Store in a well-ventilated place, container well-sealed. Carefully collect remainder, as hazardous waste.

12. Conclusions

The evaluation of different volatile binding media (VBM) has yielded promising results, particularly for menthol and cyclododecanone (CDNONE), which exhibit behavior similar to cyclododecane (CDD), but with faster and slower sublimation respectively. Cyclododecanol (CDNOL) is very slow in subliming, hence its use may be envisaged only for long-term consolidation and/or very hot climates, where the high flash point is an additional advantage (138°C). Camphene is extremely fast in subliming, hence any use is necessarily limited to very cold climates and very quick operations, also due to its low flash point (26°C).

The investigated VBM mixes allowed to obtain "tunable" properties, exhibiting intermediate properties between the starting VBM. Hence, it seems possible to select the most appropriate temporary consolidant for the target application and for the specific climatic conditions.

Certain mixtures have shown potential as temporary consolidants, such as:

• mixtures of CDD and Menthol, which exhibited a rapid sublimation process, making it a favorable option for temporary consolidation applications, although the strong dependence on environmental temperature must be considered

• mixtures of CDNONE and CDNOL, allowing to obtain intermediate sublimation speeds, proportional to the mass ratios of the components, and uniform mass loss with time.

The porosity of the substrate seems to play a role in slowing down the sublimation, as expected, likely due to some penetration of the melted consolidants. Temperature and relative humidity of the air are further parameters to be taken into account when selecting a temporary consolidant.

A limited set of tests were successfully carried out on real artifacts and architectural surfaces with the VBM investigated in this project. However, further assessment and validation of the individual VBM and their mixtures are necessary before their practical implementation in the field.

13. Open access publications on the VOLATILE4ARCHAEO project's results

The following paper are under publication in peer-reviewed interntional journals in the open access form:

- Hamada Sadek Kotb, Andrea Saccani, Elisa Franzoni, "Volatile Binding Media for Temporary Consolidation of Cultural Heritage materials: Characterization of Alternatives to Cyclododecane", in press
- Hamada Sadek Kotb, Andrea Saccani, Jean-Marc Vallet, Elisa Franzoni, "New materials for temporary consolidation of cultural heritage: investigating single and blended volatile binding media", in press
- Hamada Sadek Kotb, Jean-Marc Vallet, Elisa Franzoni, "Assessment of the effectiveness and compatibility of volatile binding media for temporary consolidation cultural heritage materials", in press.

14. Bibliography on volatile binding media

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