Lead white darkening in Old Master drawings stored in the National Gallery of Denmark (SMK)

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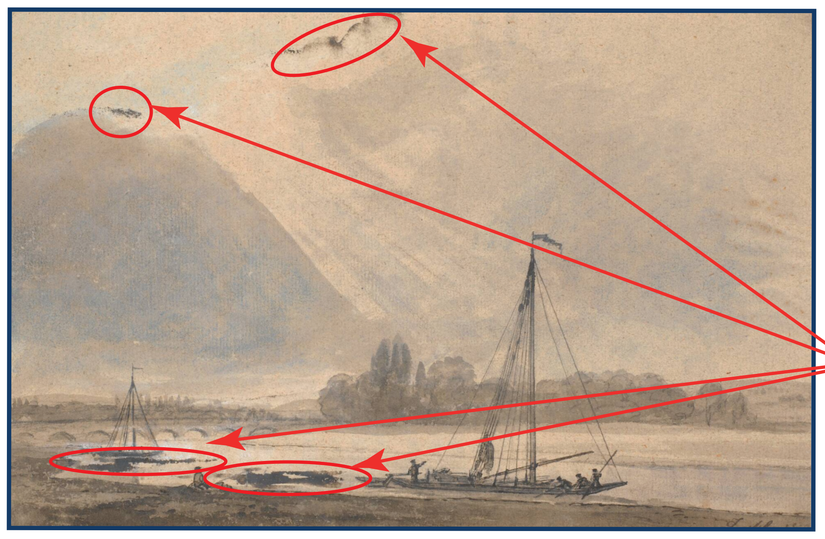
Introduction:

In recent years, **lead white darkening** was discovered on works of art in the Royal Collection of Graphic Art of the National Gallery of Denmark (SMK) in Copenhagen. This phenomenon was observed in prints, drawings and other works of art on paper containing lead white highlights and produced between the 15th and the 19th centuries. The urgency of understanding this phenomenon was underlined by the formation of newly blackened regions over a relatively short period of 10 years.



J.C. Dahl
Title - View of the Elbe near Dresden
(1824)

Blackening of lead white containing highlights

Methodology:

In order to understand and prevent the blackening phenomenon that occurs in SMK, the Lead Mad project (identifying **LEA**d compounds and why they **D**arken in white highlights in **MA**ster **D**rawings) was initiated with a consortium of 10 partners. 41 designs were chosen and multiple analytical techniques such as macro-XRF, macro-XRPD and Raman will be used to understand the reasons behind the blackening of the highlights painted with lead white. 41 designs were chosen and multiple analytical techniques such as macro-XRF, macro-XRPD and Raman will be used to understand the reasons behind the blackening of the highlights painted with lead white.

Research goals:

- To understand why some of the lead white highlights in *Old Master* drawing retain their light tones while others darken
- To identify physicochemical properties of lead white and storage conditions that increase the tendency of lead white to blacken
- To prevent the darkening of drawings with intact white highlights

Resuming table :

Sample	Calcite $CaCO_3$	Hydrocerussite $2PbCO_3.Pb(OH)_2$	Cerussite $PbCO_3$	**Galena PbS**	Cinnabar HgS	**Anglesite $PbSO_4$**
Simil-Caravaggio	X	X	X	-	-	**X**
View of the Elbe near Dresden	X	X	-	**X**	-	-
The hug	-	X	X	-	X	**X**
KKSGB140007-1	X	X	-	-	-	-
KKSGB140007-2	X	-	-	-	-	-
KSGB17770	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Inv. No. 1949	-	X	-	**X**	-	-
Inv. No. 1968	-	-	-	**X**	-	-
KKS7443_05	X	X	X	**(X)**	-	-
KKS7443_07	X	X	X	**X**	-	-
KKSgb4950	X	X	-	**X**	-	-
KKSgb7770_04	-	-	-	-	-	-

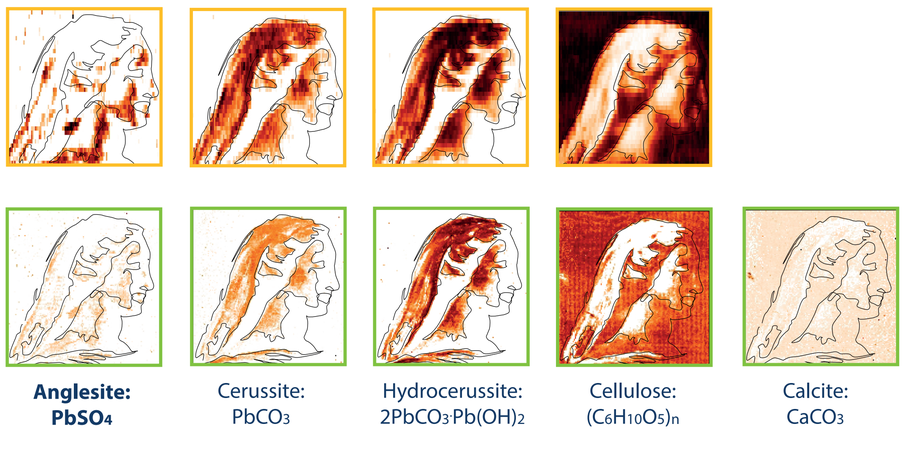
Summary table showing the crystalline compounds identified in 12 historical samples analyzed within this project. If a compound has been detected it is marked with an X, when in doubt it is marked with an (X). If a compound was not detected, it is marked with a -.

Results:

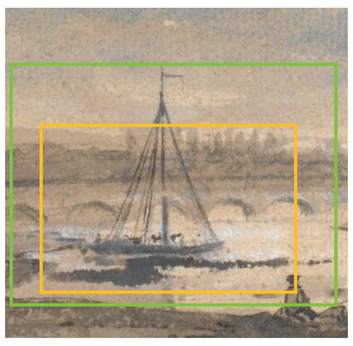
Detail of
Simil Caravaggio
??

Reflection geometry
Map size: 35x40 mm²
Step size: 1x0.3 mm²
Acquisition time: 5 s/pixel

Transmission geometry
Map size: 40x41 mm²
Step size: 0.3x0.3 mm²
Acquisition time 2 s/pixel



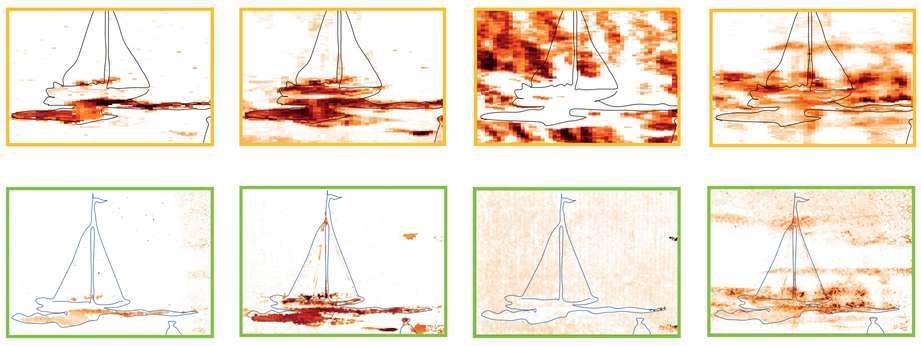
Anglesite: $PbSO_4$ | Cerussite: $PbCO_3$ | Hydrocerussite: $2PbCO_3{\cdot}Pb(OH)_2$ | Cellulose: $(C_6H_{10}O_5)_n$ | Calcite: $CaCO_3$



Detail of
View of the Elbe near Dresden
J.C. Dahl (1824)

Reflection geometry
Map size: 50x30 mm²
Step size: 1x0.3 mm²
Acquisition time: 5 s/pixel

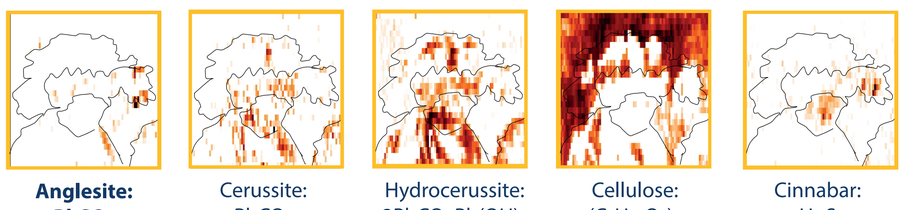
Transmission geometry
Map size: 68x50 mm²
Step size: 0.3x0.3 mm²
Acquisition time 2 s/pixel



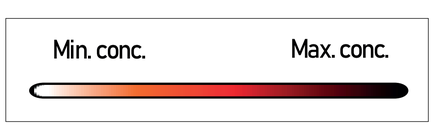
Galena: PbS | Hydrocerussite: $2PbCO_3{\cdot}Pb(OH)_2$ | Cellulose: $(C_6H_{10}O_5)_n$ | Calcite: $CaCO_3$

Detail of
??
Niclas Lavreince

Reflection geometry
Map size: 25x24 mm²
Step size: 1x0.3 mm²
Acquisition time: 5 s/pixel



Anglesite: $PbSO_4$ | Cerussite: $PbCO_3$ | Hydrocerussite: $2PbCO_3{\cdot}Pb(OH)_2$ | Cellulose: $(C_6H_{10}O_5)_n$ | Cinnabar: HgS



Conclusion:

In the drawing entitled *View of the nearby Elbe Dresden*, black **galena (PbS)** has been identified together with hydrocerussite, this can be considered the cause of the blackening of the areas originally painted with lead white. Furthermore, **galena** has also been identified in cross sections taken from heavily discolored areas and reported in the summary table, reinforcing its primary role in the blackening of white areas. The identification of **anglesite ($PbSO_4$)** in two samples must be investigated, however together with **galena** strongly suggests that the degradation of this drawings is triggered by a large presence of sulfur; the identification of cinnabar (HgS) can represent a source for this. Macro-XRPD analyzes proved to be a valuable tool for detecting and discriminating the formation of secondary compounds (and possibly tertiary such as **anglesite**) developed from the intentionally applied pigments.

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