

Pigments in Forensic Geology

Pigments are the coloring agents mixed with a vehicle to make coating such as paints, inks, and cosmetics

The vehicle is the binding agent and in paints is usually an oil such as linseed oil, or acrylic, resin, casein, wax, gum, honey, egg yolk, and egg whites. In inks the binding agent is commonly iron gall, water with gum arabic, and soluble resin. In cosmetics the binder are waxes and oils

PowerPoint Presentation by J. C. Crelling, Southern Illinois University

Pigments in Forensic Geology

OCHRE

- Ochre is a mineral that has been sought and used by humans even before homo sapiens came into existence
- It has been used as:
 - Body paint
 - Artist paint
 - Sun blocker
 - Medicine (antiseptic and clotting agent)
 - Possible religious symbol for blood, life, etc

Pigments in Forensic Geology



OCHRE

- Naturally occurring minerals:

Hematite Fe_2O_3

Magnetite Fe_3O_4



Limonite $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$

Pigments in Forensic Geology

OCHRE: Evidence for Mining

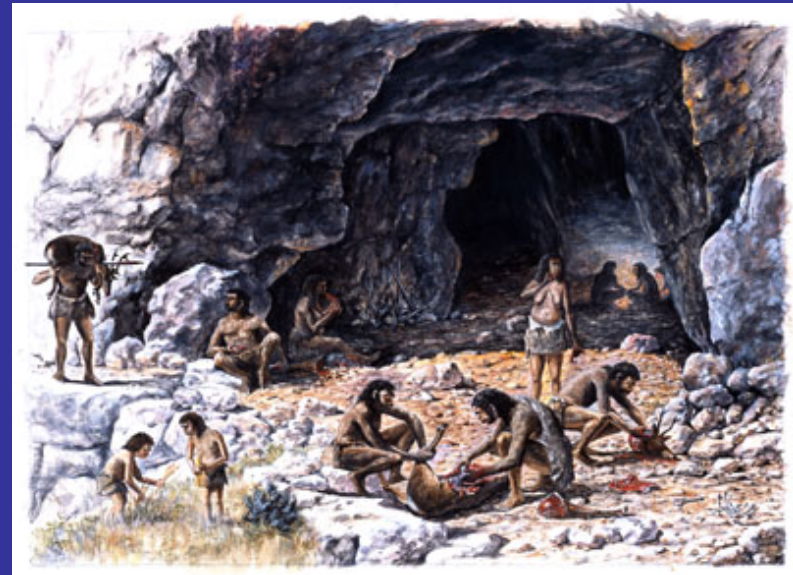
Ochre sticks (crayons) have been found in the graves of *homo erectus* dating to 1.5-1.6 million years



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OCHRE: Evidence for Mining

- 350,000 - 400,000 years ago at Wonderwerk cave, S. Africa , –ochre with hand axes
- Terra Amata site, France ochre with hand axes



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OCHRE: Evidence for Mining

- 250,000 - 200,000 years ago at Hunsgi in Southern India
- 120,000 years ago at Lion Cave , Swaziland. This is probably the oldest mine in the world.



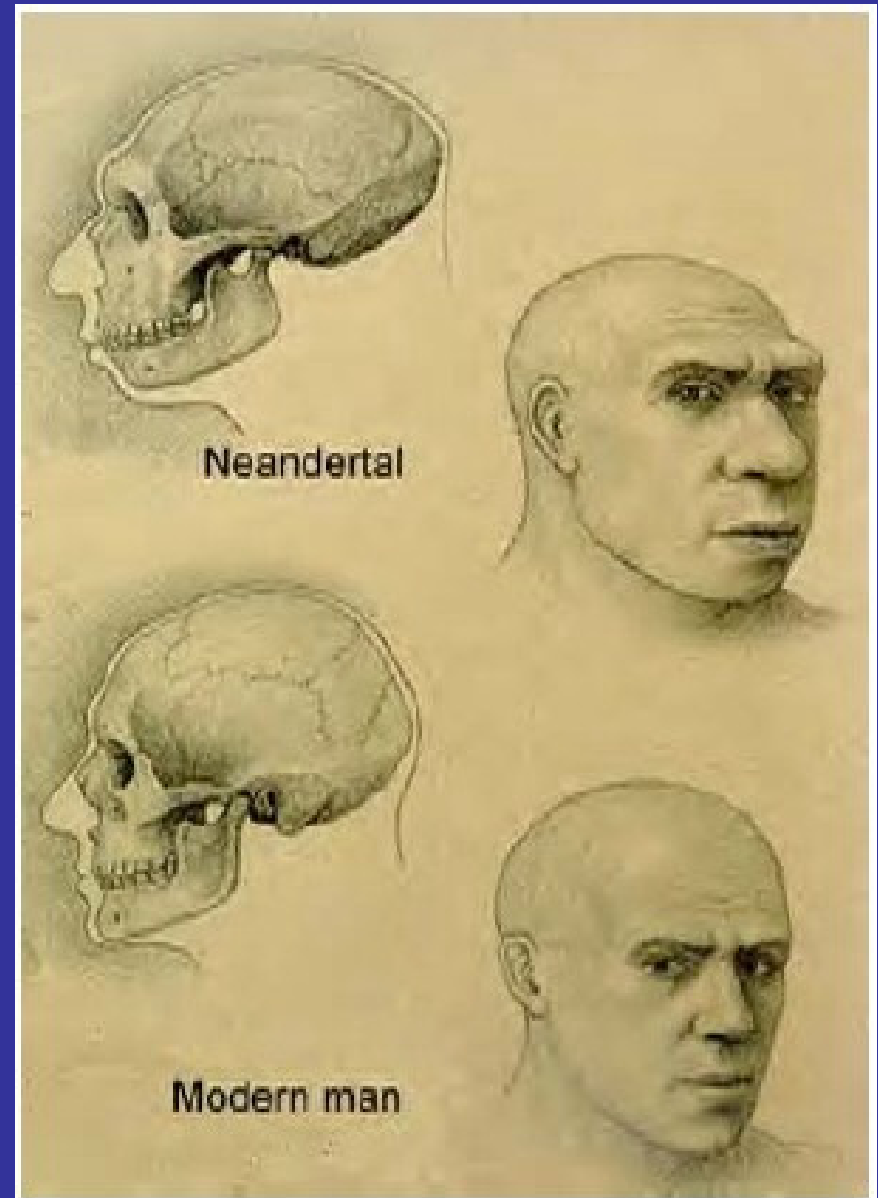
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OCHRE: Evidence for Mining

Neanderthal Man

150,000 – 32,000 ybp

- Pech de l'Aze , France
- La Chapelle-aux-Saints, France



Pigments in Forensic Geology

Prehistoric Cave Paintings

Pigments Used

Charcoal, lampblack (soot) C

Pyrolucite, MnO

Hematite, Fe₂O₃

Magnetite, Fe₃O₄

Limonite, Fe₂O₃ *H₂O

There is good evidence that in the cave paintings that many of the colors were a mixture of various pigments, and at the some sites there is evidence that ochre was calcined (heated) to get other colors

~35,00 -10,000 ybp

Homo Sapiens



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Prehistoric Cave Paintings



Pigments in Forensic Geology

Prehistoric Cave Paintings



Pigments in Forensic Geology

Mineral Pigments in Use from Ancient thru Medieval Times

Hematite

Magnetite

Limonite

Goethite

Malachite

Azurite

Cinnabar

Chrysocolla

Lapis Lazuli

Realgar

Orpiment

Cinnabar

Verdigris (copper acetate - Ancient Greek)

Van Dyke Brown (17th century peat extract)

Pigments in Forensic Geology



OCHRE

- Naturally occurring minerals:

Hematite Fe_2O_3

Magnetite Fe_3O_4



Magnetite

Limonite $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$

Pigments in Forensic Geology

Goethite $\text{FeO}(\text{OH})$



Cinnabar HgS



Pigments in Forensic Geology



Malachite $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$

Azurite $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$



Pigments in Forensic Geology

Lapis Lazuli



Chrysocolla



Lapis Pigments

Michelangelo

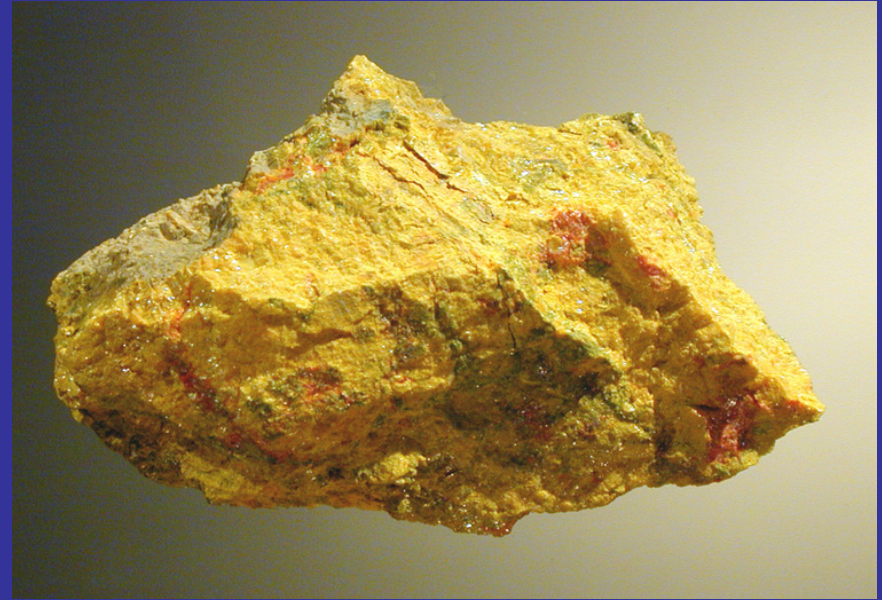


Vermeer



Pigments in Forensic Geology

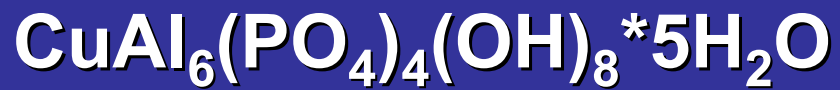
Orpiment As_2S_3



Realgar AsS

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Turquoise



Pigments in Forensic Geology

- The pigments described above were also used in Dark Age and Medieval illuminated manuscripts
- Because these mineral pigments are already oxidized or otherwise stable at surface conditions they retain their original brilliance even today

† Johannes Baptista †













omne labia
mea aperies.
Et os meum



Pigments in Forensic Geology

Some Dye Pigments in Use from Ancient thru Medieval Times

Indigo – blue

Woad – blue

Pomegranate – yellow

Madder – orange yellow

Saffron – yellow orange

Murex - purple

Note: all dyes used were natural vegetable dyes until 1856 when Perkin developed the first aniline dye from coal tar. This was a major achievement and the beginning of organic chemistry

Pigments in Forensic Geology

Some Pigments Uses in Cosmetics

Ancient

Iron Oxides

Galena PbS (eye shadow)

Malachite (eye shadow)

Cerrusite PbCO_3

Modern

Titanium Dioxide (yellow)

Iron Oxides

Mica (pearlescent agent)

Bismuth Oxychloride (pearlescent agent)

Pigments in Forensic Geology

- Because many of the pigments are minerals standard geological techniques such as microscopy, X-ray diffraction, SEM analysis, and optical spectroscopy can be used to discriminate them
- The organic vehicle or binders can be discriminated by Gas Chromatography – Mass Spectrometry

Pigments in Forensic Geology

Thus, any paint, inks, cosmetics etc. involved in a criminal case can be examined and used as potential evidence

Locard Case

- In 1912 a bank clerk Emile Gourbin in Lyons, France was suspected of the strangulation murder of his girlfriend, Marie Latelle, but he had a good alibi
- Edmond Locard took scrapings from under Gourbin's fingernails and analyzed them



Locard Case

- He found rice starch and magnesium stearate (binders?) with bismuth, zinc oxide, iron oxide, Venetian red pigment
- He then found a druggist in Lyon who had mixed these same ingredients in a custom face powder for Marie Latelle
- When confronted with the evidence Gourbin confessed



Pigments in Forensic Geology

Dates of First Use for Paint Pigments

Oripment (yellow)	ancient
Red Ochre	ancient
Smalt (cobalt blue)	1550
Van Dyke Brown	1690
Prussian Blue	1704
Alizarin (Madder)	1830
Zinc White	1850
Titanium White	1920
Manganese Blue	1950

Gardner Museum Case

- On 18 March 1990 two white male dressed as Boston Police Officers stole 13 paintings worth over \$300 million
- The investigation went cold until two men offered to be intermediaries in getting the paintings back. They offered a few paint chips reportedly from one of the Rembrandt's as evidence that they were in contact with the thieves



Gardner Museum Case



- **Walter McCrone the head of the famous McCrone labs in Chicago examined the paint chips. He concluded that the paint was consistent with those used by Rembrandt but would not confirm that they were indeed Rembrandt's**
- **The case is still unsolved and the 13 paintings are still missing**

1500 Forgeries

- In 1985 a trunk containing ~pastels drawings by the modern Russian painter Larionov was discovered
- Larionov left Russia for France in 1915 and these paintings were apparently left behind and forgotten
- When some 200 of these paintings were exhibited in Germany in 1987 some questions about their authenticity were raised



1500 Forgeries

- A few of the paintings were sent to the McCrone Labs
- They were examined by optical microscopy and SEM X-ray analysis
- The paintings were found to have pure rutile TiO_2 as a pigment which was not used until at least 1940, thus the paintings were produced after that year and not before 1915 as purported



The Case of the Vineland Map

- **In 1957 a manuscript “The Vineland Map and the Tartar Relation was offered for sale in Geneva, Switzerland. It was bought by a rare book dealer who sold it to the Yale University library**
- **The startling thing about the map dated at 1440 was that it showed North America 52 years before the first voyage of Columbus**

Handwritten notes at the top left of the page, including the number '111' and some illegible text.

Deinde de post tempore in die...
etiam in eadem die...
etiam in eadem die...
etiam in eadem die...



Septentrionalis

Thule ultima

Tartaria fluvius

Etiam non sicut...
etiam non sicut...
etiam non sicut...

In hoc...
In hoc...
In hoc...

Castellus
Hic...
Hic...

Etiam...
Etiam...
Etiam...

Commodus

Ingeniosus

Castellus

Indica

Per...
Per...
Per...

Finis Ethiopiae

Disceat uocari in nomine dei
ostea uisus inuolucra uide
17026 W



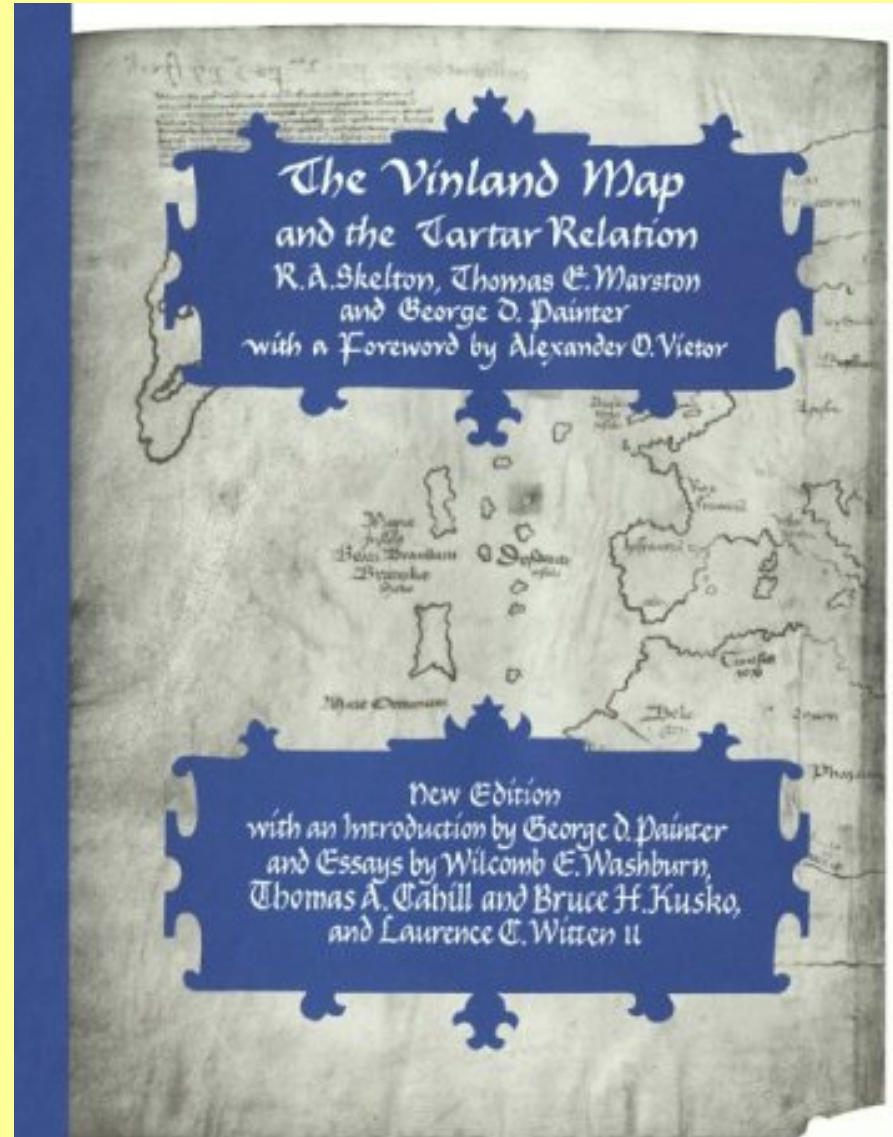
Crete
17026 W

in Hungaria Cyrbodan^{iste} adhuc con-
tra Soldanum Damasa pliatu
si in terra tartarorum remanserat
ajango Coten Syrenen. et alij
quam plures quos nominare non
opporret octodaj vero cum esset
fortis multitudinis tres ex pa-
tris exercitus ordinauit. p^o
prefecit Zati filium fratris et
misit ad occidentem contra ec-
clesiam dei et omnes prouincias
occidentis Qui ueniendo sub-
iugauit terram alij polsam
terram byzemenorum. Hii tar-
tarem erant comamca loqu-
tes Cepit Ibidem etiam fortis-
simam ciuitatem nomine Baz-
chin licet cum bello ductu
no. Alia uero ciuitas ponte
se reddidit nomine Jakme
qua de re ciuitatem non de-
seruit sed acceptis spolijs
et miterstis ut ut moris eo-
rum est nobilibus alijs
hominibus ciuitatem locans
Incolas transire fecit et pro-
cepit aduersus omnia ciui-
tatem maximam repleta sa-
ms. s. Gazaris et alams. nec
non et alijs fauorem parauit
Diuesorum Est autem sita
super fluum magna habente
partem maris et q^{ue} transibat
ciuitatem tartari obsidentes
in superiori parte fluum
diuiserunt aquam ad ipse

et submerferunt ciuitatem
cum omnibus que in se ciuitas
continebat preterea Isac tunc
temporis subiugauit terram
celzomen et terram traugita-
rum atq^{ue} magnam camomam
necnon et ursum et captakp
oma metropoli ruse ciuitate
maxima et nominatissima
per stratem multam p^{ro}loru
et bellam plurima que ad
p^{ro}ns transeo quia scriptore
exunt p^{ro}cialem Cinnij fili-
us octodaj patris Zati
qui modo est cum reuersus
est p^{ro} occulte mtitu intel-
lecto in reditu autem cepit
terram Gazareum terra
et alanorum postea terra
et et ad ultimum terram
tardatorem Iste sunt terre
p^{ro}id^{em} noz sed Diuesorum
p^{ro}iomatum et posite sunt
ad meridiem iuxta maze
Hys anno ad terram p^{ro}id^{em}
est reuersus Zati uero er-
m in rusia contra pilacos id est
bulgarum magna et mordu-
ans et captis eis suis eos
exercitui subiugauit / Ex-
tunt postea processit contra
polomam et hmgariam et
in p^{ro}q^{ue} exercitui sumetis
terravum cum fr^{atre} suo
adu misit contra poloma
decem milia pugnatorum
ex quibus in terre p^{ro}imario

The Case of the Vineland Map

- Yale published the manuscript in 1965 and it was an instant best seller and a book-of-month club selection
- A new edition is still in print



The Case of the Vineland Map

**The map was immediately questioned
and then studied intensely**

Points putting the map in the 15th century

- 1. The binding**
- 2. The paper**
- 3. The paleography (writing style)**
- 4. Radiocarbon dating (1434+/- 11years)**
- 5. PIXIE analysis of ink**

The Case of the Vineland Map



Points questioning the authenticity of the map:

- 1. McCrone analysis finding anatase a titanium mineral not in use until recently**
- 2. A separate analysis by Raman spectroscopy showing the ink lines with a yellow line containing anatase under the carbon line**