THE ROLE OF ORGANIC POLLUTANTS IN THE ALTERATION OF HISTORIC SODA SILICATE GLASSES

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ALTERATION of GLASS COLLECTIONS

Survey of the National Museums of Scotland (NMS) glass collection

- widespread alteration of part of the collection
- mainly 19-20th century British, Islamic and Chinese collections

Crystalline deposits
Crizzling = micro cracks
Cracking and flaking

Glass disintegration
INVESTIGATION of the CAUSES
Analyses and monitoring

- **GLASS COMPOSITION**
  - Stable: high sodium / potassium and high calcium content
  - Unstable: high sodium and low calcium (or lead) content

- **RELATIVE HUMIDITY (RH)**
  - Winter months: low RH (down to 15 % RH)
  - Summer months: high RH (up to 65 % RH)

- **CRYSTALLINE DEPOSITS**
  - Sodium formates

- **ORGANIC POLLUTANTS**
  - Main: acetic acid (1700-2800 µg/m³)
  - Minor: formic acid (190-420 µg/m³) and formaldehyde (260-960 µg/m³)

What is the role of organic pollutants in alkali glass alteration?

Is formaldehyde responsible of alteration?

Why do we observe only formate when acetic acid is major?

Do organic pollutants have an effect on the glass structure?

What are the mechanisms?

Do organic pollutants influence the alteration kinetics?

**QUESTIONS to ANSWER**

Accelerated and ambient AGEING EXPERIMENTS

Replica of 17th Venitian glass: high-soda, low-lime silicate
AGEING EXPERIMENTS

ACCELERATED AGEING
- Temperature: 60 ºC
- 100 % RH
- High pollutant concentration

1-8 weeks

ANALYSES
- Crystalline deposits: Raman spectroscopy
- Glass structure: SEM-EDS & Raman

LONG TERM CHEMICAL STRUCTURE & MECHANISMS

AGEING EXPERIMENTS

ACCELERATED AGEING
- Temperature: 60 °C
- 100 % RH
- High pollutant concentration

AMBIENT AGEING
- Ambient temperature
- Ambient RH
- Real pollutant concentration
- Static conditions

1-8 weeks

ANALYSES
- Crystalline deposits: Raman spectroscopy
- Glass structure: SEM-EDS & Raman

LONG TERM CHEMICAL STRUCTURE & MECHANISMS

13 months

ANALYSES (every 4 weeks)
- Crystalline deposits: Raman spectroscopy
- Glass chemical structure: dynamic SIMS

MECHANISMS & KINETICS

**CONTROLLED ATMOSPHERE**
- Temperature ~ 19 °C ± 2 °C
- RH : 48 ± 2 %
- Atmosphere: ambient air, nitrogen, formic acid or formaldehyde

**MUSEUM CONDITIONS**
- Fluctuating RH and temperature
- High concentration of all three pollutants

2 NMS stores: cellars
- Elemental concentration variation as a function of depth.
- Resolve concentration variation for depths between 10 nm to 2-3 µm → Alteration in ambient conditions

**Analytical conditions**
- Primary beam: O\(^{-}\) at 60 nA
- Impact energy: 10 keV
- Glass sample gold coated
- Vacuum: 10\(^{-9}\) torr
- Secondary ions: Na\(^{+}\), K\(^{+}\), Ca\(^{2+}\), Mg\(^{2+}\), Al\(^{3+}\), H\(^{+}\), Si\(^{4+}\)

- During alteration, only alkali ions are depleted
- Hydrated layer formed
GLASS SURFACE APPEARANCE

NON ACIDIC (ALKALINE) ENVIRONMENT
Ambient air, Nitrogen, Formaldehyde

- Fine droplets
- Dendritic crystals

ACIDIC ENVIRONMENT
Formic acid and Cellars

- Mostly sodium formate droplets or crystals

AMBIENT AGEING

- Ambient storage
  - Transparent, fine cracks
- Dry storage
  - Strong cracks, lifted scales

ACCELERATED AGEING

- Ambient storage
  - Iridescences → thin layer
  - Porosity
- Dry storage
  - Thick opaque layer
  - Strong cracking

- Formaldehyde effect similar to nitrogen in the first stages and then ambient air → Cannizzaro reaction
- Cellars’ alteration = acids alteration
- Cracking and flaking similar to NMS objects
The acidity amplifies the leaching of sodium:
• in depth
• within altered layer

Structure of altered glass of NMS objects:
alkali depleted and hydrated = acidic alteration

Cellars’ alteration = formic acid alteration
With time, sodium depletion advances in depth

= follow the sodium depletion depth

**SODIUM DEPLETION DEPTH**

SODIUM DEPLETION DEPTH
Sodium extraction increases linearly with RH / number of water layers at the surface

Formic acid vapour greatly increases the amount of sodium leached from the glass
Formic acid accelerates the leaching reaction in soda silicate glass

Formaldehyde does not affect the leaching reaction
Formic acid + RH/T fluctuations = alteration kinetics linear
- alteration progress ~ 2 nm per day

Cellars = formic acid alteration kinetics
- No minimum acid concentration: vapours saturate the water film!

Time estimated to reach the decanter altered layer thickness ~ 50 years
CONCLUSION - Part I
Mechanisms

SODA SILICATE GLASS

- Alkaline solution build up
- Selective leaching of alkali
- Congruent dissolution
- Hydrated gel layer
- Polymerisation
- New amorphous structure

Non-polluted atmosphere, formaldehyde

- Alkaline solution build up
- Formaldehyde
- \( \text{CO}_2, \text{SO}_2 \)
- Salt crystallisation at the surface
- Alteration slows down

Organic acid pollutants

- Formic acid
- RH and temperature fluctuations
- Continuous leaching reaction

- Enhance alkali leaching
- Silanols polymerisation
Formaldehyde is inert to the glass as it solely reacts with the sodium leached by the humidity and might actually be beneficial as it neutralises NaOH avoiding dissolution of the glass.

Formic acid modifies the alteration of soda silicate glasses and acts on the
- **Mechanisms**: FA acidifies the water film as a result the leaching reaction dominates
  The combination of RH/T fluctuation maintains a continuous leaching of the alkali
- **Structure**: FA induces the formation of hydrated and alkali depleted layer, which cracks at low RH
- **Kinetics**: FA accelerates the leaching reaction by approximately 10 times

In mixed pollutant environment, FA dominates in the water film because of its high acid ionisation constant.

Formic acid is responsible for the accelerated alteration of the unstable NMS glass collections.

NEW NMS GLASS STORAGE

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