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

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ARCHAEOLOGY | CONSERVATION SCIENCES | PALAEONTOLOGY | PALAEO ENVIRONMENTS
IPANEMA ANCIENT MATERIALS RESEARCH PLATFORM

UNIVERSITE PIERRE & MARIE CURIE
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THE UNIVERSITY OF EDINBURGH

ALTERATION of GLASS COLLECTIONS

British vase, 19-20th

Chinese vase 19-20th

Islamic bottle 19-20th century

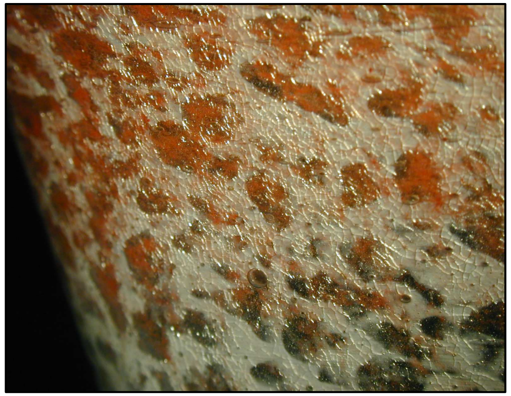
Photos copyright NMS

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

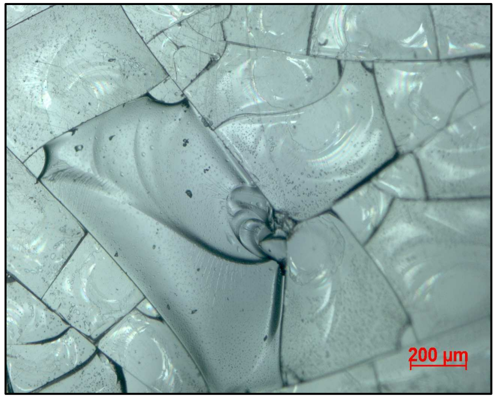
- widespread alteration of part of the collection
- mainly 19-20th century British, Islamic and Chinese collections

Crystalline deposits

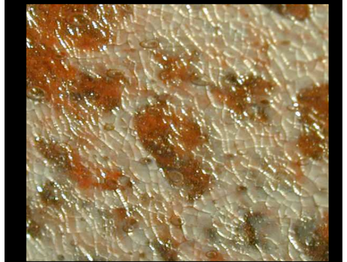
Crizzling = micro cracks

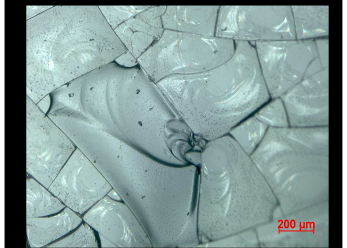


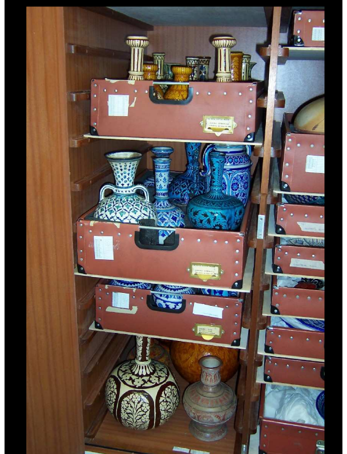
Cracking and flaking



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/m^3)
  - Minor: formic acid (190-420 µg/m^3) and formaldehyde (260-960 µg/m^3)

Emitted by wooden cabinets

Robinet L., Eremin K., Cobo del Arco B., and Gibson L. T., Journal of Raman Spectroscopy 35 (2004) 662

QUESTIONS to ANSWER

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

Is formaldehyde responsible of alteration ?

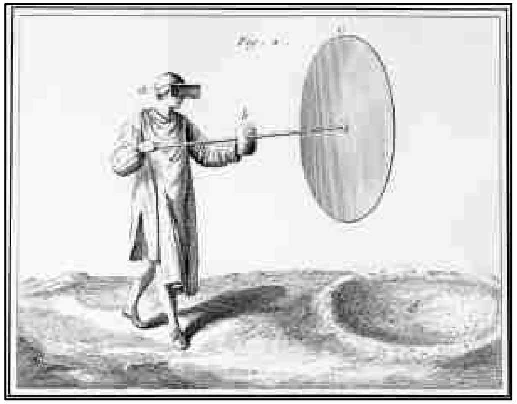
Why do we observe only formate when acetic acid is major ?

Do organic pollutants have an effect on the glass structure ?

What are the mechanisms ?

Do organic pollutants influence of the alteration kinetics ?

Accelerated and ambient
AGEING EXPERIMENTS



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

AGEING EXPERIMENTS

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

1-8 weeks

<u>ANALYSES</u>
- Crystalline deposits: Raman spectroscopy
- Glass structure : SEM-EDS & Raman

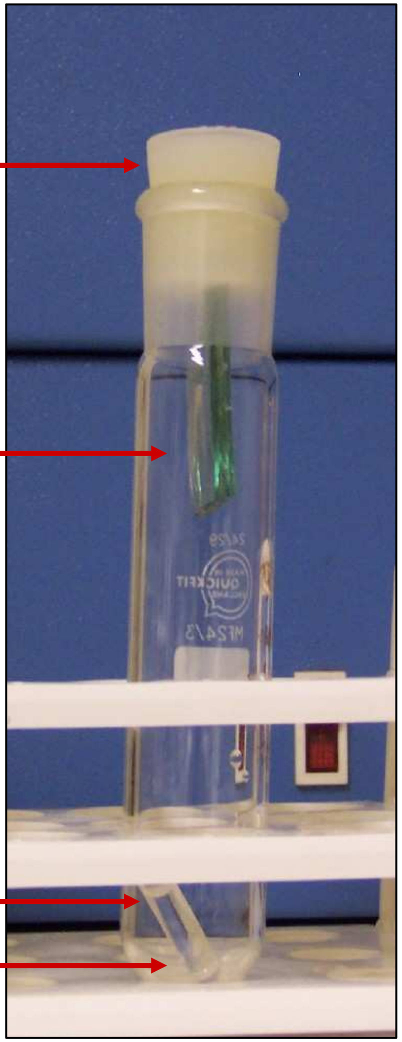
LONG TERM CHEMICAL STRUCTURE & MECHANISMS

Silicone stopper

glass fragment

Distilled water

pollutant



Robinet L., Coupry C., Eremin K., Hall C., and Lacome N., Journal of Non-Crystalline Solids 353 (2007) 1546

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ANALYSES

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LONG TERM CHEMICAL STRUCTURE & MECHANISMS

AMBIENT AGEING

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

Controlled atmosphere
dessicators

Museum conditions
storage cabinet

13 months

ANALYSES (every 4 weeks)

- Crystalline deposits : Raman spectroscopy
- Glass chemical structure : dynamic SIMS

MECHANISMS & KINETICS

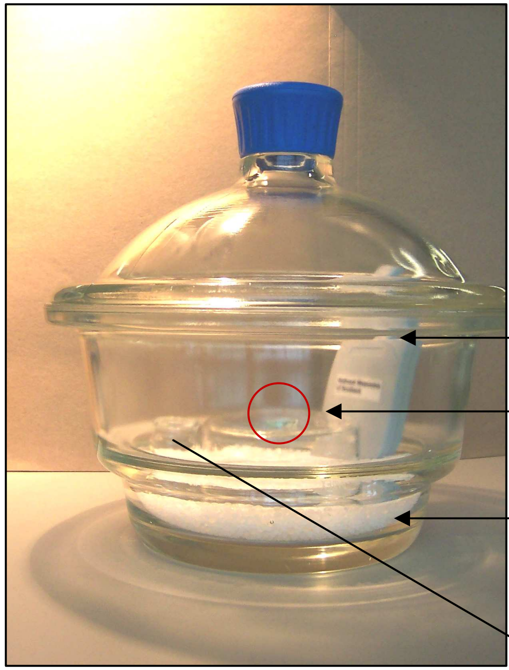
L. Robinet, C. Hall, K. Eremin, S. Fearn, J. Tate; Journal of Non-Crystalline Solids 355 (2009) 1479.

AMBIENT AGEING

CONTROLLED ATMOSPHERE

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

Desiccators



RH/T sensor

Glass fragment

Artsorb
to control the RH

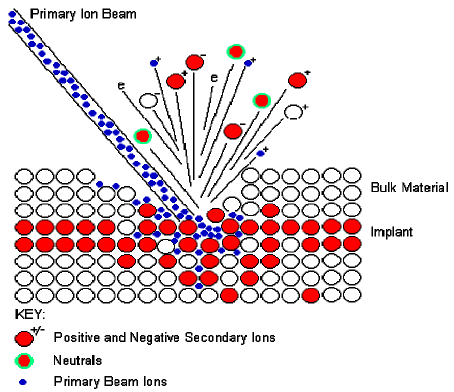
Pollutant

MUSEUM CONDITIONS

- Fluctuating RH and temperature
- High concentration of all three pollutants

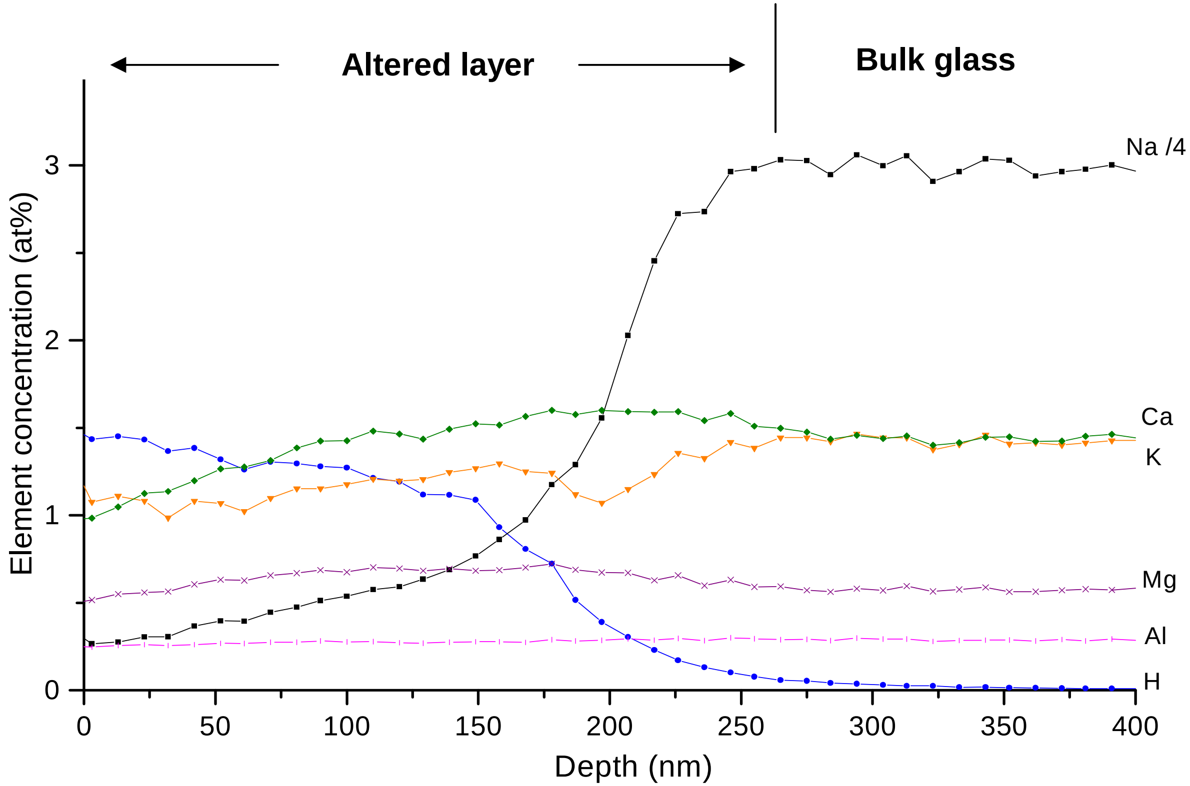
2 NMS stores: cellars

SIMS ELEMENTAL DEPTH PROFILE



- 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+}



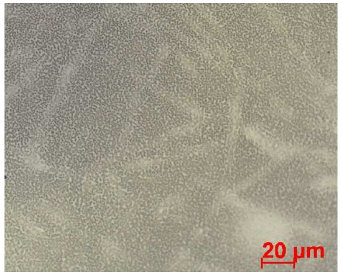
- During alteration, only alkali ions are depleted
- Hydrated layer formed

GLASS SURFACE APPEARANCE

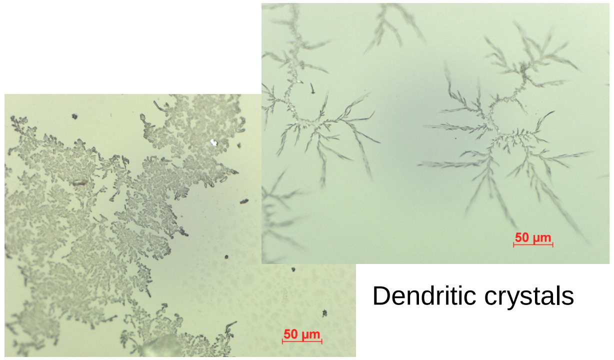
AMBIENT AGEING

NON ACIDIC (ALKALINE) ENVIRONMENT

Ambient air, Nitrogen, Formaldehyde



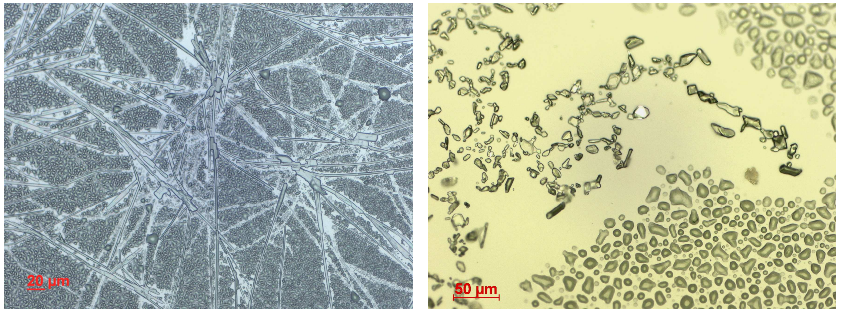
Fine droplets



Dendritic crystals

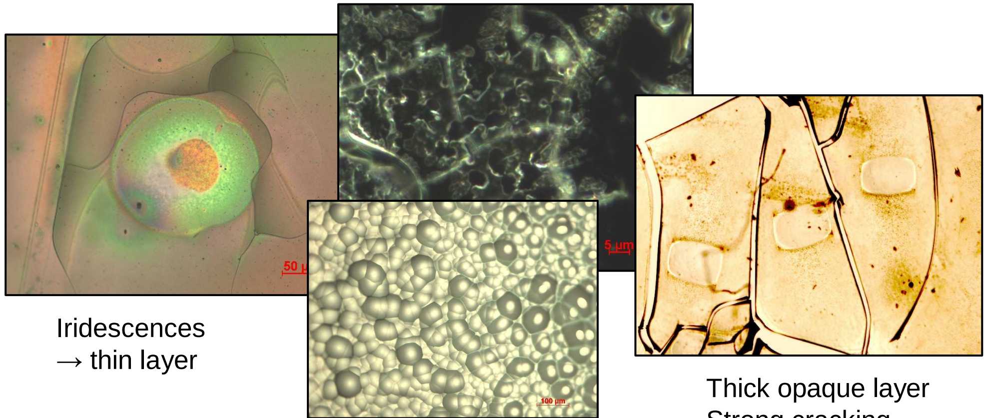
ACIDIC ENVIRONMENT

Formic acid and Cellars



Mostly sodium formate droplets or crystals

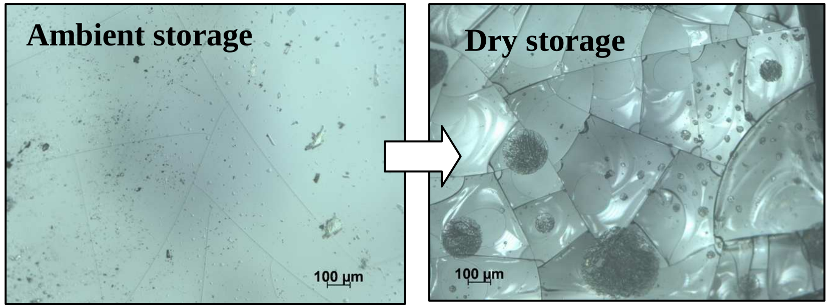
ACCELERATED AGEING



Iridescences
→ thin layer

Porosity

Thick opaque layer
Strong cracking



Transparent, fine cracks

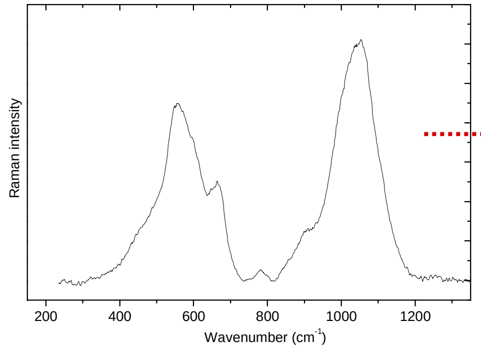
Strong cracks, lifted scales

- Formaldehyde effect similar to nitrogen in the first stages and then ambient air → Cannizarro reaction

- Cellars' alteration = acids alteration
- Cracking and flaking similar to NMS objects

CHEMICAL STRUCTURE

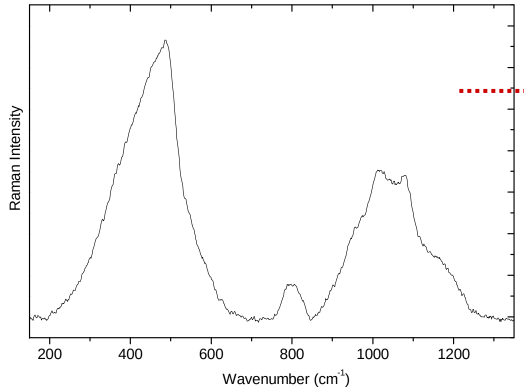
ACCELERATED AGEING



New amorphous hydrated material

NON ACIDIC

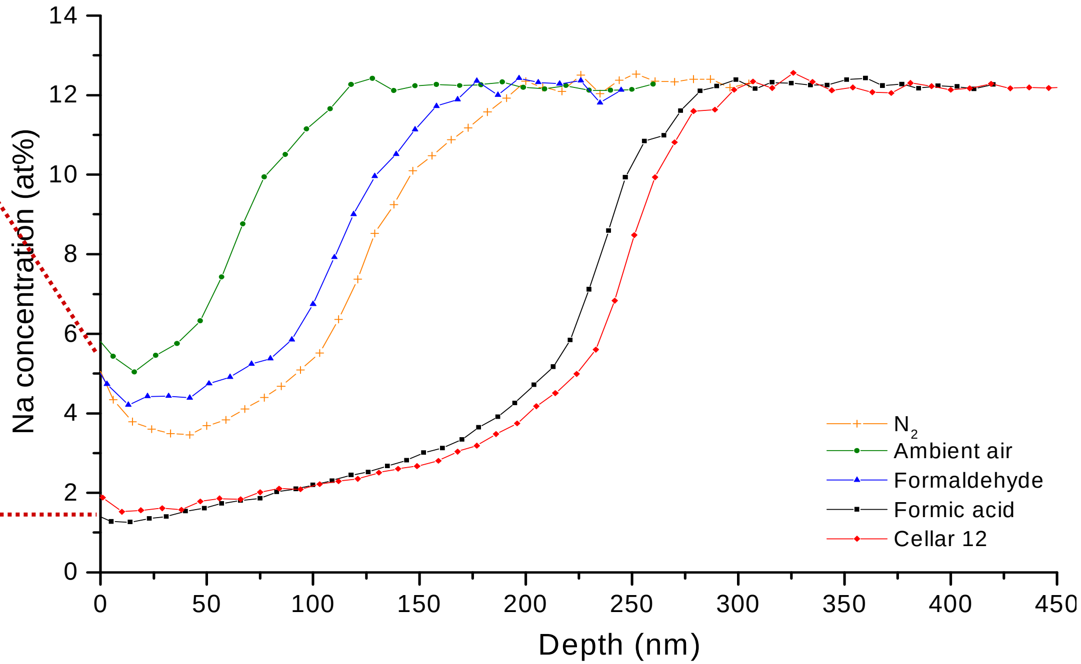
ACIDIC



Hydrated layer deprived in alkali

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

AMBIENT AGEING

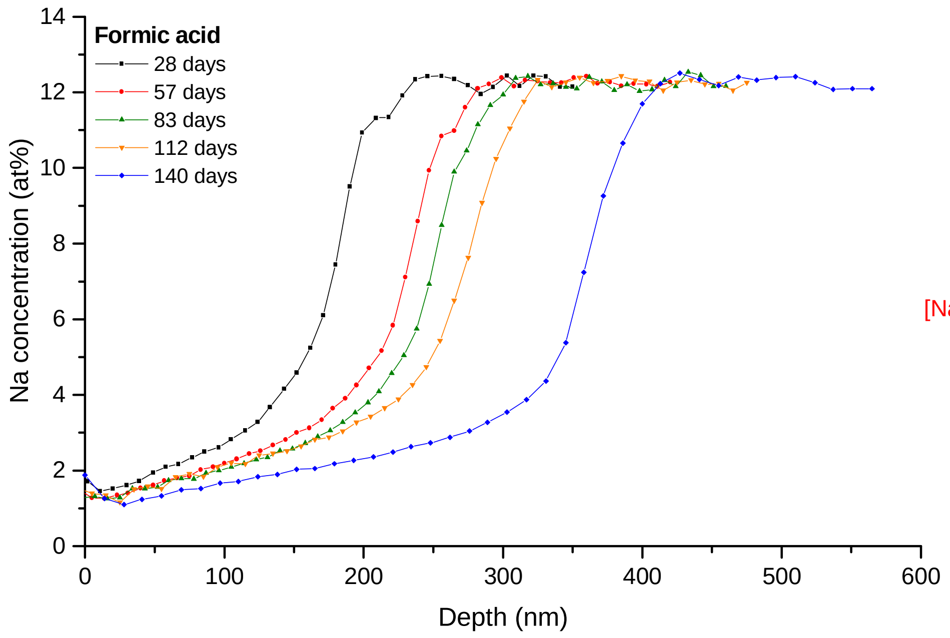


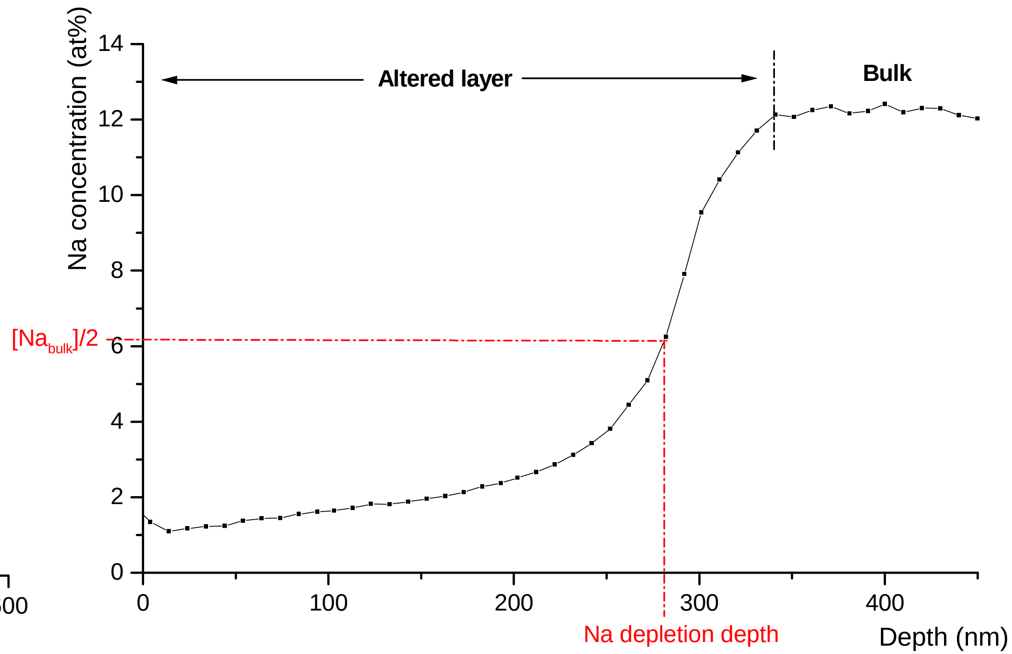
- ➢ The acidity amplifies the leaching of sodium:
  - in depth
  - within altered layer
- ➢ Cellars' alteration = formic acid alteration

SODIUM DEPLETION DEPTH

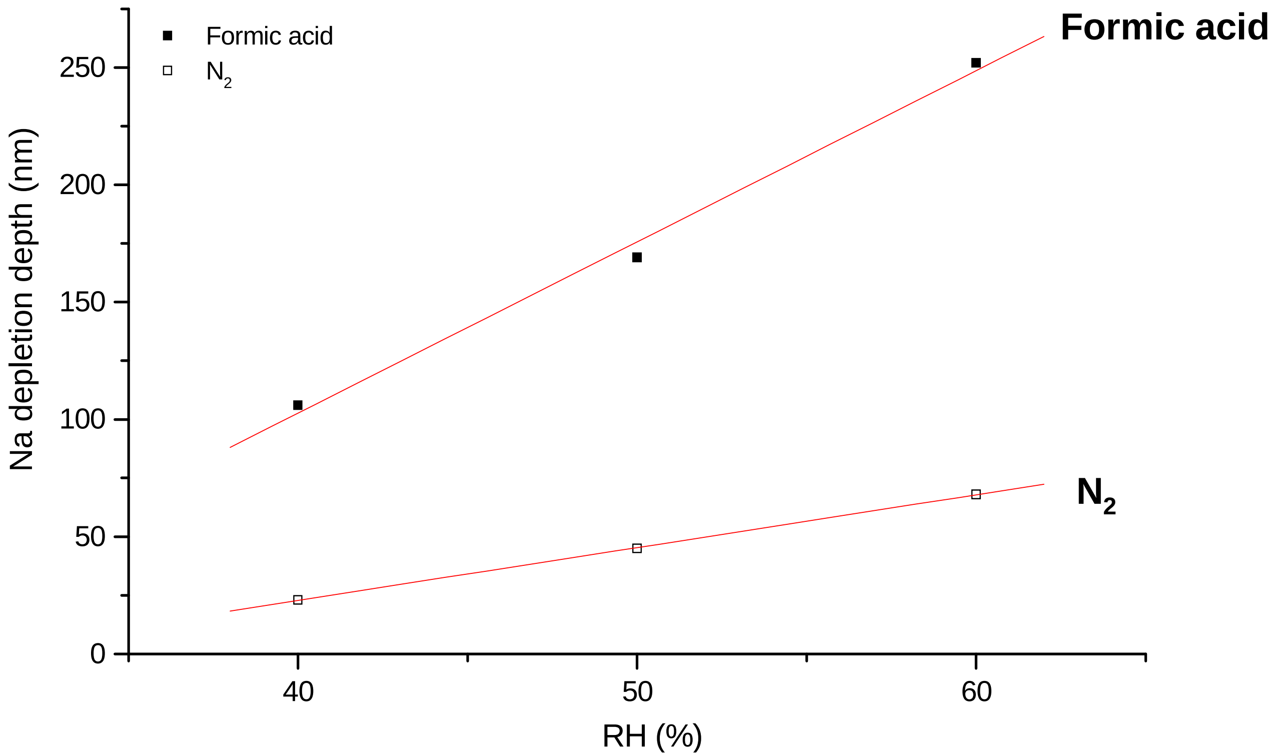
**With time,
sodium depletion advances in depth**

**Alteration progress
= follow the sodium depletion depth**



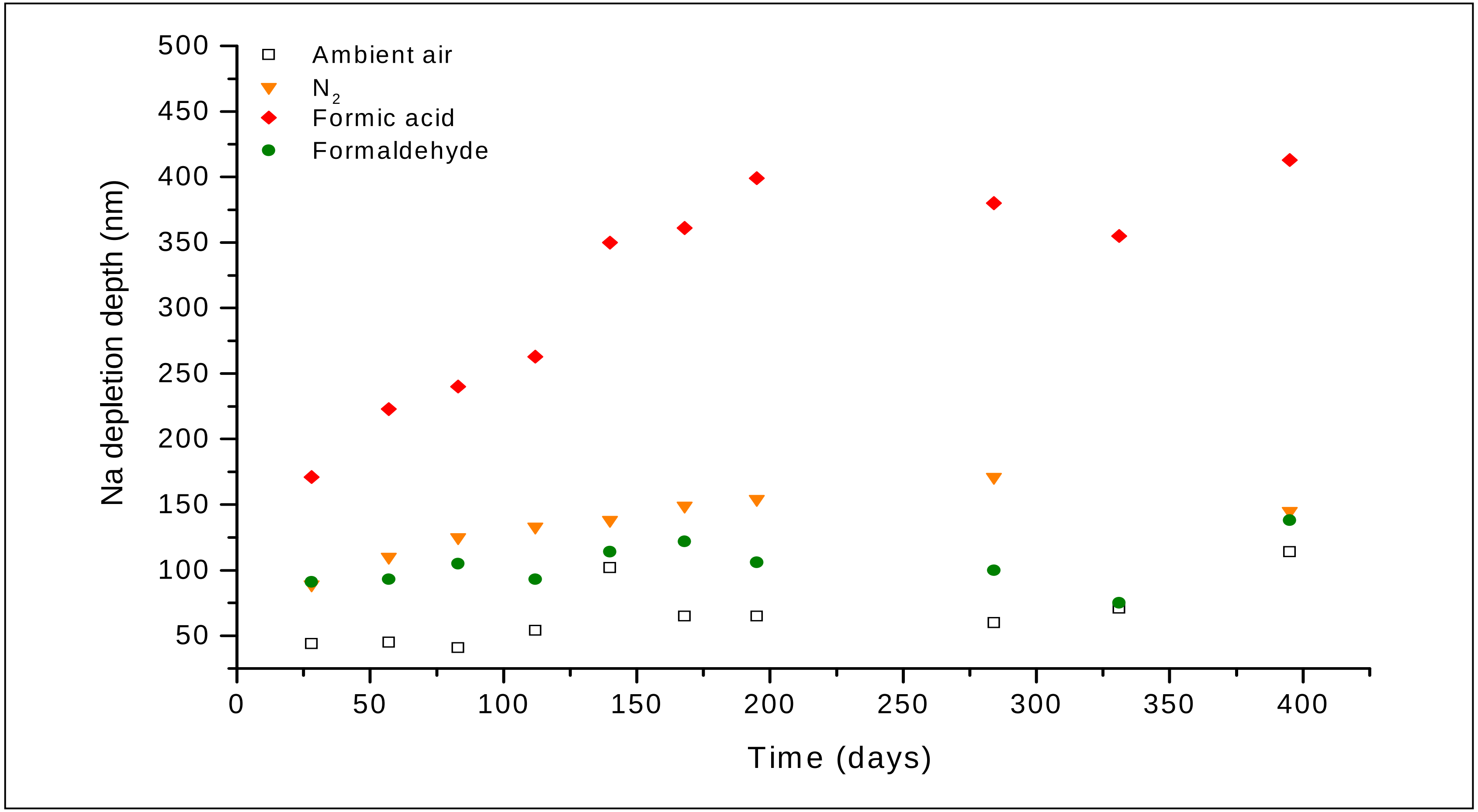


EFFECT of RH and ACID POLLUTANTS



- ➢ 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

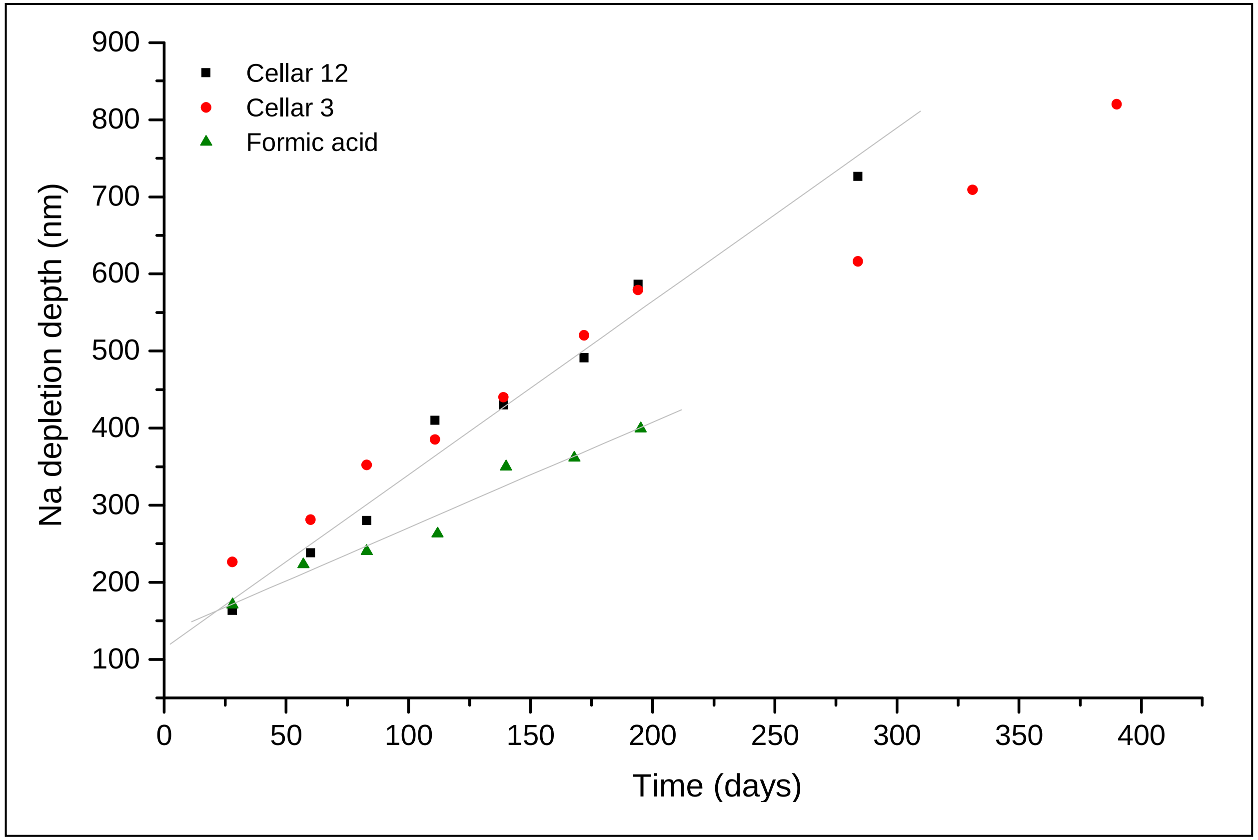
KINETICS of ALTERATION



- **Formic acid** accelerates the leaching reaction in soda silicate glass
- **Formaldehyde** does not affect the leaching reaction

KINETICS of ALTERATION

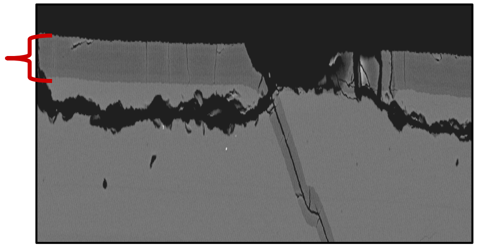
AGEING EXPERIMENTS



NMS COLLECTIONS

British glass decanter,19th century

37 µm



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

humidity

Selective leaching of alkali

Non-polluted atmosphere, formaldehyde

Organic acid pollutants

Formic acid

Alkaline solution build up

- Enhance alkali leaching
- Silanols polymerisation

Formaldehyde
CO_2, SO_2

RH and temperature fluctuations

Congruent dissolution
Hydrated gel layer

Polymerisation
New amorphous structure

Salt crystallisation at the surface

Alteration slows down

Continuous leaching reaction

CONCLUSION – Part II
Answers to Questions

➢ **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 results 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 approximatly 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

L. Robinet, C. Hall, K. Eremin, S. Fearn, J. Tate; Journal of Non-Crystalline Solids 355 (2009) 1479.

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