ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

Analysis of ancient materials and their degradation – Lecture 5

MSE-482

Prof. Dr. Claire Gervais

Content

1. Introduction to Materials
   - Materials: definitions, multidisciplinarity, challenges
   - The triangle Structure-Property-Function
   - Materials research: Why, What, How, Where?

2. Introduction to ancient materials
   - Diversity of ancient materials: paintings, archaological objects, fossils, ivory, ceramics.
   - What is ancient? The concept of materials history and impact on their scientific study
   - Typical reasearch topics in ancient materials

3. Analyzing ancient materials: key concepts
   - Heterogeneity in materials: a fuzzy concept with clear consequences.
   - Too big or not too big? The art of adapting measurement scale to property scale.
   - Sample preparation: bulk, cross-sections, thin-sections, porous materials.
   - Example: Embedding techniques for thin sections of brittle paint samples.

Content

4. Synchrotron techniques for ancient materials
   - Synchrotron light: generation and specificities
   - A specific synchrotron technique: X-ray absorption spectroscopy
   - Example: Degradation of smalt pigment in paintings

5. X-ray tomography techniques: Going to 3D and 4D imaging
   - Materials through the X-ray beam: attenuation coefficients
   - Acquiring a 3D image: Acquisition and reconstruction (principles)
   - Basics of image processing: filtering, segmentation, labelization
   - Example: Virtual unfolding of ancient manuscripts

6. Physico-chemistry of materials degradation
   - Reproducing and accelerating natural aging: limits of validity.
   - In-situ analysis of degradation processes.
   - Radiation damage: how to evaluate it and minimize it.
   - Example: Radiation damage of Prussian blue paper artworks

Assignment – Correction

Assignment: Read following article

Investigation of the Discoloration of Smalt Pigment in Historic Paintings by Micro-X-ray Absorption Spectroscopy at the Co K-Edge

Laurianne Robinet,[*,†] Marika Spring,[‡] Sandrine Pagès-Camagna,[§] Delphine Vantelon,[‖] and Nicolas Trcera[‖]

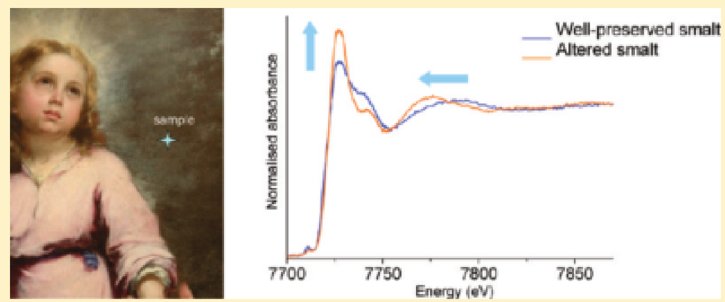
[†]IPANEMA, Synchrotron SOLEIL, Saint Aubin, BP48 F-91192 Gif-sur-Yvette Cedex, France

[‡]National Gallery, Scientific Department, Trafalgar Square, London WC2N 5DN, U.K.

[§]Centre de Recherche et de Restauration des Musées de France, Palais du Louvre, F-75001 Paris, France

[‖]Synchrotron SOLEIL, LUCIA Beamline, Saint Aubin, BP48 F-91192 Gif-sur-Yvette Cedex, France

ABSTRACT: Smalt was commonly used as a pigment by artists between the 16th and 18th centuries. It is a powdered blue potash glass colored by cobalt ions and often degrades causing dramatic changes in the appearance of paintings. The aim of the work presented in this paper was to investigate the changes in the structure and environment around the cobalt ion on deterioration, to further our understanding of the basis of the loss of color. Particles of well-preserved and altered smalt in microsamples from paintings in the National Gallery, London, and the Louvre, Paris, were analyzed using synchrotron micro-X-ray absorption spectroscopy at the Co K-edge. X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) measurements showed that in intense blue particles the cobalt is predominantly present as Co^{2+} in tetrahedral coordination, whereas in colorless altered smalt the Co^{2+} coordination number in the glass structure is increased and there is a shift from tetrahedral toward octahedral coordination. The extent of this shift correlates clearly with the alkali content, indicating that it is caused by leaching of potassium cations, which act as charge compensators and stabilize the tetrahedral coordination of the cobalt ions that is responsible for the blue color.



Assignment: Answer following questions

A. Locate the Why? What? Where? and How?

Give lines and pages or highlight in color the pdf
Answer to each with a short paragraph If it is not clear in the publication, tell it!

B. Choice of technique

Explain link between technique and question to answer
e.g.: Technique X chosen because sensitivity to structural feature / spatial / non-destructive / ...etc.

C. Statistics and representativity

How did they handle statistical significance?
Give lines and pages or highlight in color the pdf

D. Explain **one** experiment

From sample preparation to...
Data acquisition to...
Data processing

Assignment – Part A

A. Locate the Why? What? Where? and How?

Give lines and pages or highlight in color the pdf
Answer to each with a short paragraph If it is not clear in the publication, tell it!

Part A - WHY?

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1. Why is this topic of research important?
2. Why doing this particular study?
3. Why choosing to chose precisely this analytical strategy?

1. Smalt is a pigment that often degrades in paintings together with surrounding oil binding, causing brown discoloration and drastic changes in appearance of the painting.
2. Numerous hypotheses for the origin of color loss but exact physico-chemistry still not known.
3. Size of samples restrain the type of analytical techniques

Part A - WHY?

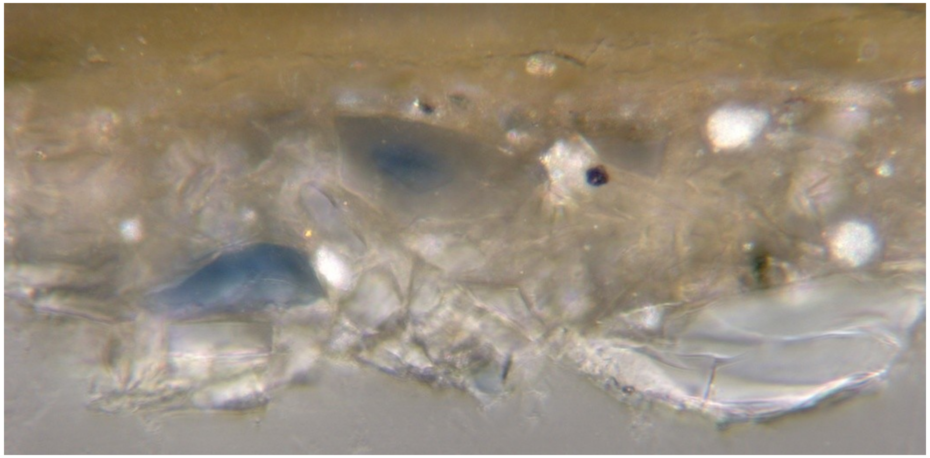
Pedro Campana, *The Conversion of the Magdalen,* c.1562, National Gallery London

Detail of Christ showing deteriorated smalt in his cloak

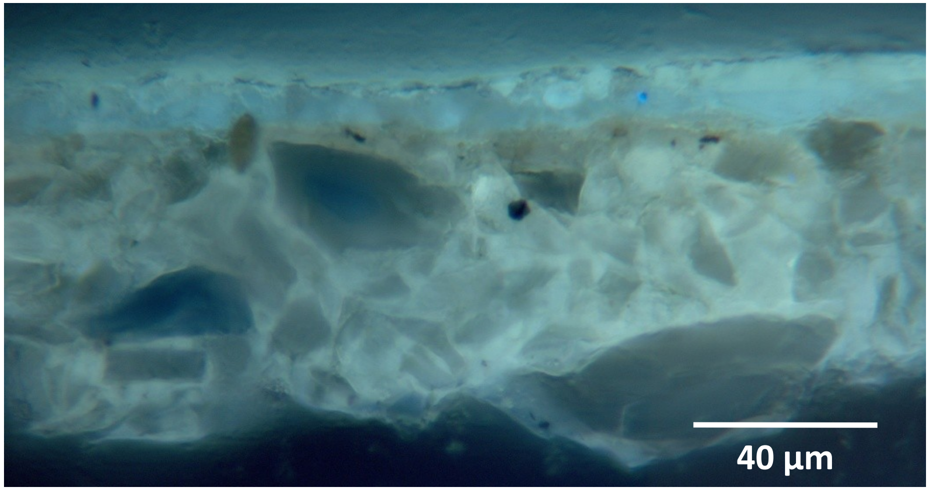
Provided by L. Robinet

Part A - WHY?

Bartolomé Esteban Murillo, *The Heavenly and Earthly Trinities,* c. 1675–82, National Gallery London



Normal light



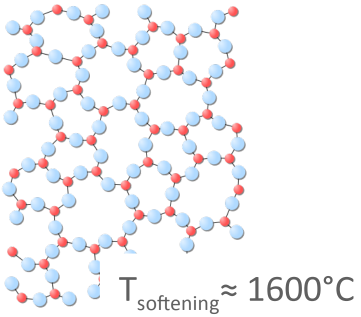
Ultraviolet light

Provided by L. Robinet

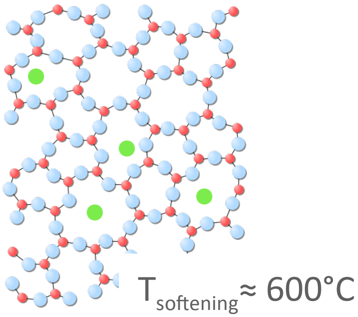
Part A - WHAT?

1. What is current knowledge about material?
2. What is current gap in knowledge?
3. What is the focus of this study?

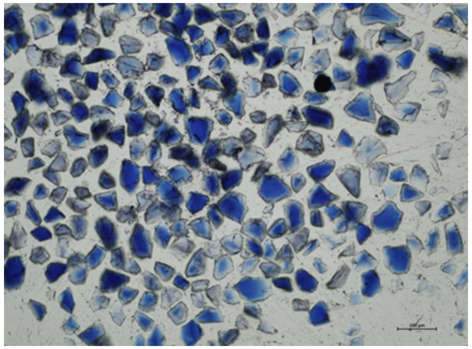
1. Smalt is a potash glass with color given by cobalt ions. Particle size, cobalt content and potassium (vs sodium) play a role on final color. Presence of other elements, including Arsenic.



Silica glass



“Potash glass” (+ K2O)



“Potash glass” + Cobalt

Discoloration observed to be correlated with yellowing of binding medium, loss of potassium from smalt particles, leached potassium that react with fatty acids to produce metal soaps

Part A - WHAT?

1. What is current knowledge about material?
2. What is current gap in knowledge?
3. What is the focus of this study?

2. Several hypotheses put forward:

- Cobalt leaching
- Cobalt speciation (tetrahedral to octahedral)
- Potassium/Cobalt ratio
- Cobalt oxidation state

But no special consensus.

Exact physico-chemical origin of the color change not fully explored.

Part A - WHAT?

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1. What is current knowledge about material?
2. What is current gap in knowledge?
3. What is the focus of this study?

3. Discoloration of smalt pigment in paintings

→ More precisely: ”exact physico-chemical origin of color change”

→ More precisely: ”Investigate further the various hypotheses”

- Cobalt leaching
- Cobalt speciation (tetrahedral to octahedral)
- Potassium/Cobalt ratio
- Cobalt oxidation state

Part A - WHERE?

1. Where do materials come from?
2. Where to measure?
3. Size(s) of samples and targeted areas?

1. Micro-samples from historic paintings considered to be representative

- Paolo Veronese, *The Consecration of Saint Nicholas* (NG 26), 1562, National Gallery, London
- Paolo Veronese, *Les Dieux de l'Olympe, 1557,* Louvre, Paris
- Paolo Fiammingo, *Landscape with the Expulsion of the Harpies* (NG5467), c.1590, National Gallery, London
- Bartolomé Esteban Murillo, *The Heavenly and Earthly Trinities* (NG 13), 1675–1682, National Gallery, London.
- François Lemoyne, *Hercule tuant Cacus*, 1718, Louvre, Paris.





Part A - WHERE?

1. Where do materials come from?
2. Where to measure?
3. Size(s) of samples and targeted areas?

1. Micro-samples from historic paintings considered to be representative
2. Measurement on both discolored and healthy areas for comparison
3. Size of micro-samples is 300-400µm with particles 10-50µm

Constraints on analytical techniques:
- non-destructive
- micro-focused
- high flux

Part A - HOW?

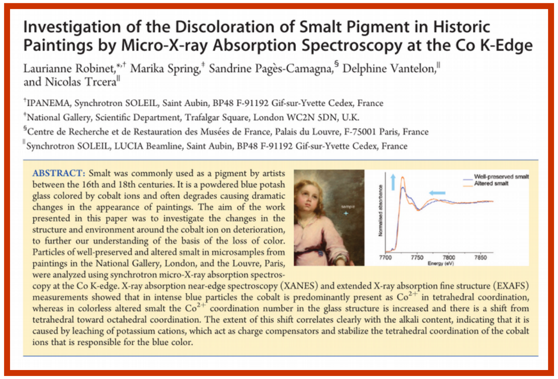
1. Which technique(s) for what ?
2. Which sample preparation and environment?
3. Which data processing and statistics?

1. According to what is the focus and size of the material:
    - Cobalt leaching: **SEM-EDX**
    - Cobalt speciation: **micro-XANES at Co-edge**
    - Potassium/Cobalt ratio: **SEM-EDX**
    - Cobalt oxidation state: **micro-XANES at Co-edge**

Complementary spectroscopy techniques also used to investigate binder (FTIR, Raman)

Part A - HOW?

1. Which technique(s) for what?
2. Which sample preparation and environment?
3. Which data processing and statistics?



Investigation of the Discoloration of Smalt Pigment in Historic Paintings by Micro-X-ray Absorption Spectroscopy at the Co K-Edge

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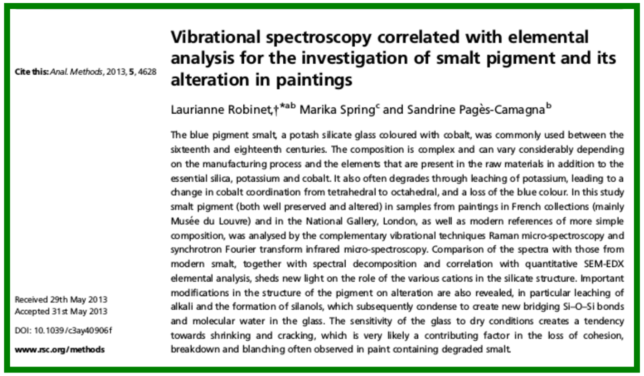
Elemental Composition
SEM-EDX



Cite this: Anal. Methods, 2013, 5, 4628

Vibrational spectroscopy correlated with elemental analysis for the investigation of smalt pigment and its alteration in paintings

Laurianne Robinet,†[*ab] Marika Spring[c] and Sandrine Pagès-Camagna[b]

The blue pigment smalt, a potash silicate glass coloured with cobalt, was commonly used between the sixteenth and eighteenth centuries. The composition is complex and can vary considerably depending on the manufacturing process and the elements that are present in the raw materials in addition to the essential silica, potassium and cobalt. It also often degrades through leaching of potassium, leading to a change in cobalt coordination from tetrahedral to octahedral, and a loss of the blue colour. In this study smalt pigment (both well preserved and altered) in samples from paintings in French collections (mainly Musée du Louvre) and in the National Gallery, London, as well as modern references of more simple composition, was analysed by the complementary vibrational techniques Raman micro-spectroscopy and synchrotron Fourier transform infrared micro-spectroscopy. Comparison of the spectra with those from modern smalt, together with spectral decomposition and correlation with quantitative SEM-EDX elemental analysis, sheds new light on the role of the various cations in the silicate structure. Important modifications in the structure of the pigment on alteration are also revealed, in particular leaching of alkali and the formation of silanols, which subsequently condense to create new bridging Si–O–Si bonds and molecular water in the glass. The sensitivity of the glass to dry conditions creates a tendency towards shrinking and cracking, which is very likely a contributing factor in the loss of cohesion, breakdown and blanching often observed in paint containing degraded smalt.

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www.rsc.org/methods

Co speciation
µ XANES and EXAFS Co K-edge

Silicate structure
Synchrotron FTIR spectroscopy
Raman spectrometry

Part A - HOW?

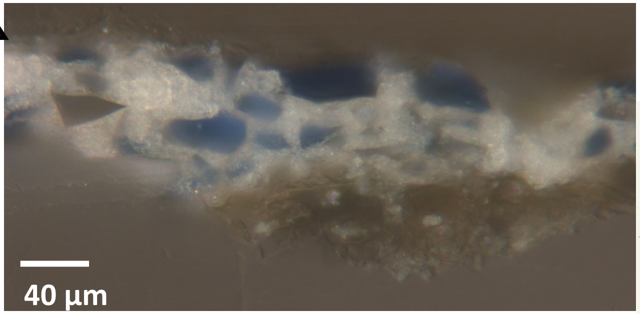
1. Which technique(s) for what?
2. Which sample preparation and environment?
3. Which data processing and statistics?

2. Microsample extracted from painting, cross-sections prepared

+

References : modern smalt powder (only K, Si, Co) + silica gel with CoCl2

Paolo Fiammingo, *Landscape with the Expulsion of the Harpies* (NG5467), c.1590, National Gallery, London



Provided by L. Robinet

Part A - HOW?

1. Which technique(s) for what?
2. Which sample preparation and environment?
3. Which data processing and statistics?

3. SEM-EDX: Average several spectra for single particle, as many particles as possible
XAS: only data collected from homogeneous particles, two scans averaged for each spectra

Part B : Choice of Technique

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B. Choice of technique

Explain link between technique and question to answer
e.g.: Technique X chosen because sensitivity to structural feature / spatial / non-destructive / ...etc.

Part B : Choice of Technique

1. Sensitivity and Specificity
2. Modalities required for the samples

Micro-X-ray Absorption Spectroscopy at Cobalt K-edge

1. Sensitive to Cobalt structural environment and oxidation state. Non-destructive and does not require a lot of sample preparation (except cross-section).

2. Spot size 4x2 microns to analyze smalt particles (range from 10 to 50 microns) + fluorescence mode because not possible to work in transmission (cross-section too thick).

Part C : Statistics and Representativity

C. Statistics and representativity

How did they handle statistical significance?
Give lines and pages or highlight in color the pdf

Part C : Statistics and Representativity

1. Representativity of the painting
2. Representativity of the sample
3. Representativity of the measurement

1. Paintings from different museums and different periods to avoid misrepresentation

2. - Micro-samples with <u>both</u> well-preserved and deteriorated smalt particles
   - Reference samples investigated too (smalt powder + silica gel)

3. - As many particles as possible in the cross-section for SEM-EDX + 6-10 locations for XAS
   - Only measurement from homogeneous particles
   - Two scans on same point measured and averaged for XAS
   - XAS: Smalt reference in transmission and silica gel in fluorescence mode to match same modalities
   - Accuracy of SEM-EDX quantitative analysis obtained with reference glass

Results

Hypotheses for Smalt degradation:

- Cobalt leaching: **SEM-EDX**
- Cobalt speciation: **micro-XANES at Co-edge**
- Potassium/Cobalt ratio: **SEM-EDX**
- Cobalt oxidation state: **micro-XANES at Co-edge**

Complementary spectroscopy techniques also used to investigate binder (FTIR, Raman)

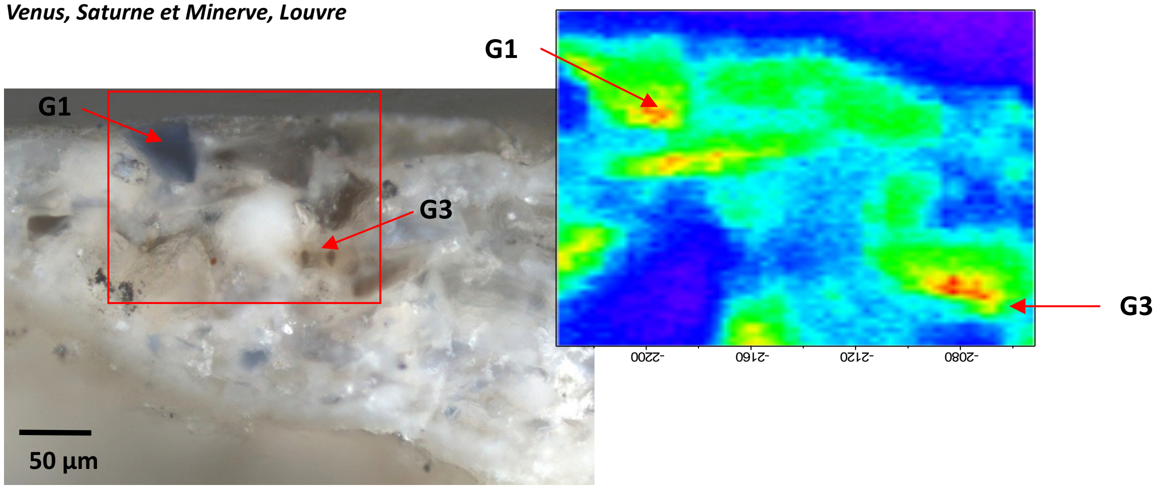
Results: SEM-EDX analysis

Paolo Veronese, *Les dieux de l'Olympe: Venus, Saturne et Minerve, Louvre*

Weight %	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	FeO	CoO	As_2O_3	NiO	PbO
G1 well-preserved	64.4	1.8	1.2	16.0	7.0	0.8	2.0	2.1	4.2	0.1	0.4
G3 altered	76.2	0.7	0.4	1.8	6.0	0.5	2.2	4.1	7.0	0.9	0.2

Altered regions: depletion of potassium

Silicon map

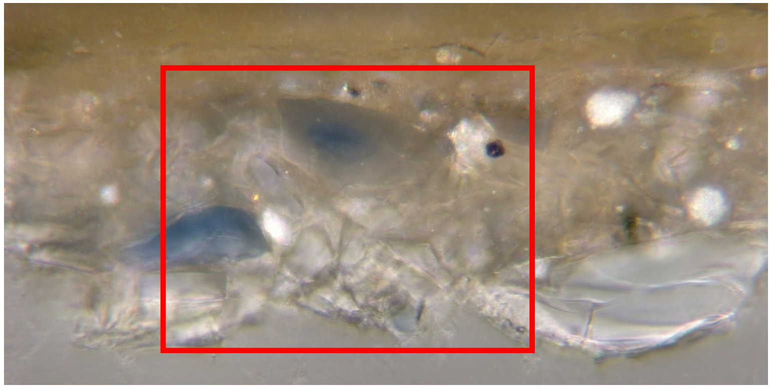


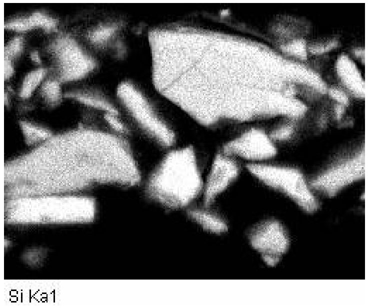
Provided by L. Robinet

Results : SEM-EDX analysis

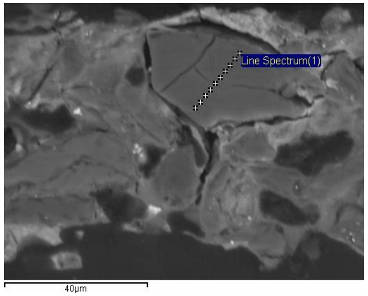
Bartolomé Esteban Murillo, *The Heavenly and Earthly Trinities, (zoom)* National Gallery London

Altered regions: depletion of potassium

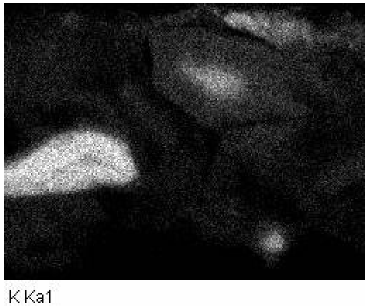




Silicon EDX map



Back-scattered image SEM



Potassium EDX map

Provided by L. Robinet

Results

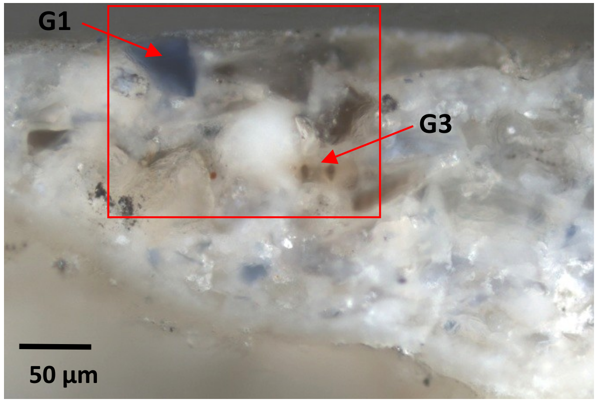
Hypotheses for Smalt degradation:

- Cobalt leaching: **No**
- Cobalt speciation: **micro-XANES at Co-edge**
- Potassium/Cobalt ratio: **Potassium leaching**
- Cobalt oxidation state: **micro-XANES at Co-edge**

Complementary spectroscopy techniques also used to investigate binder (FTIR, Raman)

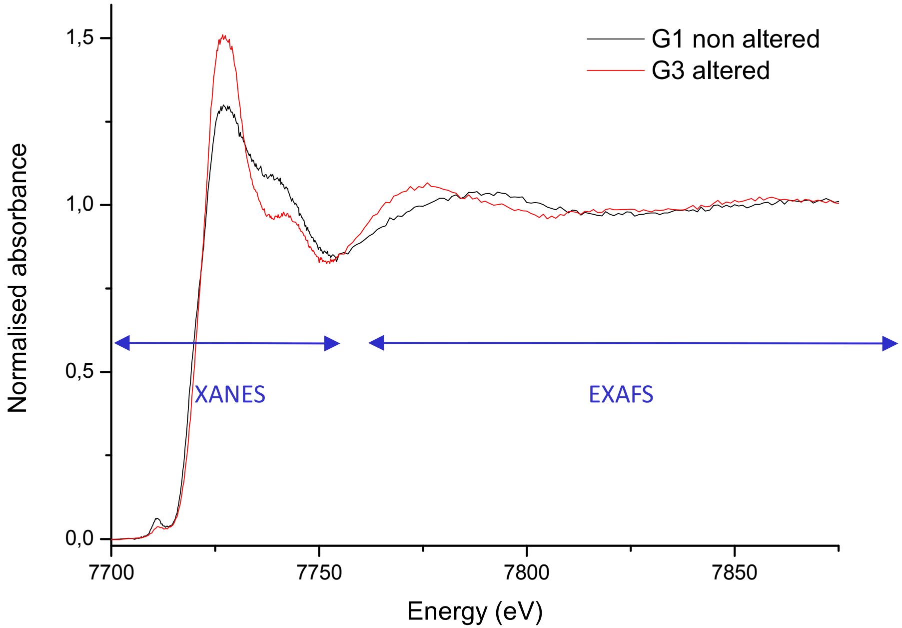
Results: micro-XAS at Co K-edge

Paolo Veronese, *Les dieux de l'Olympe: Venus, Saturne et Minerve, Louvre*



Co K-edge micro X-ray absorption spectroscopy
LUCIA beamline at SOLEIL

- Fluorescence mode
- Beam size of 4 × 2 µm



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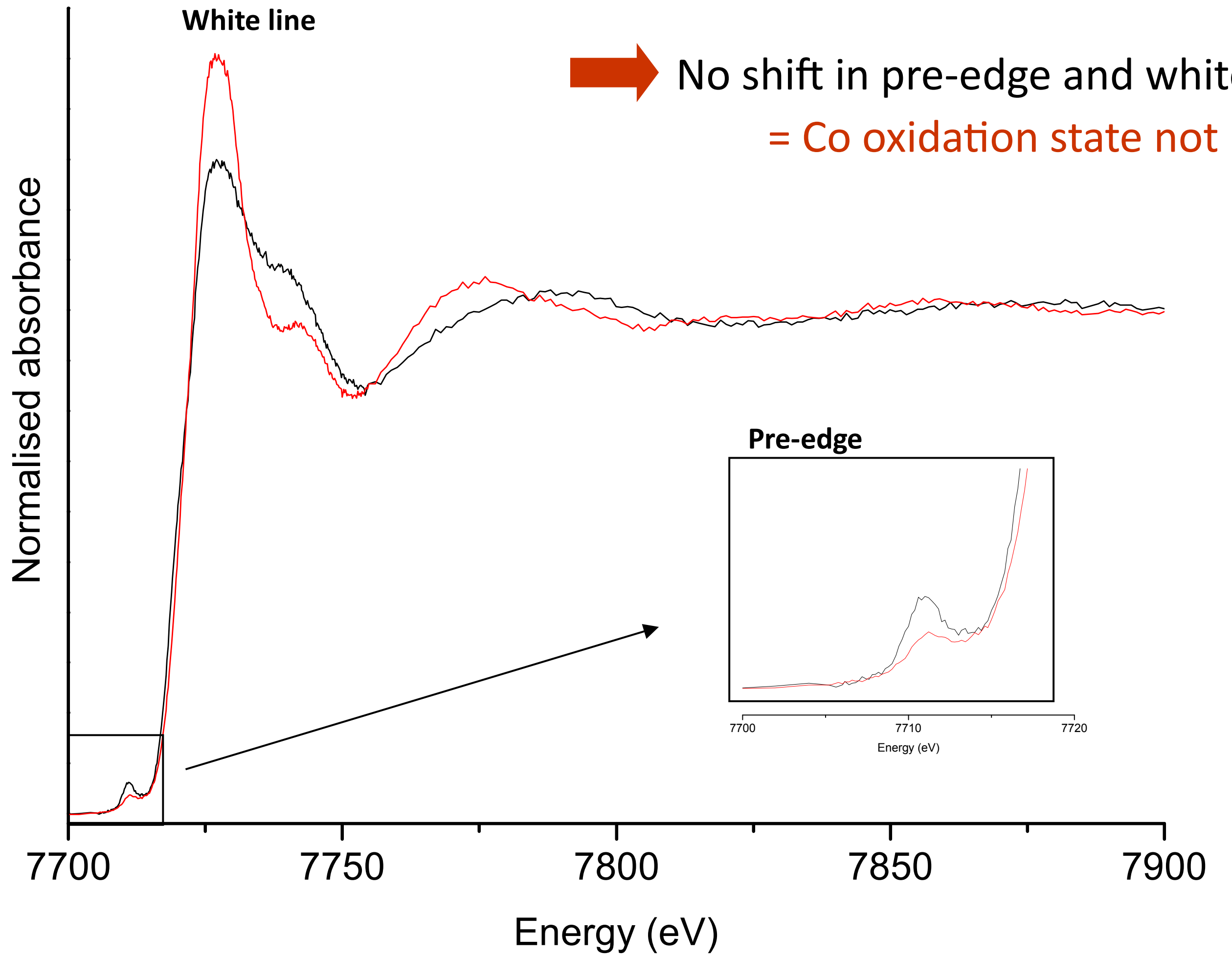
Results: micro-XAS at Co K-edge



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Results

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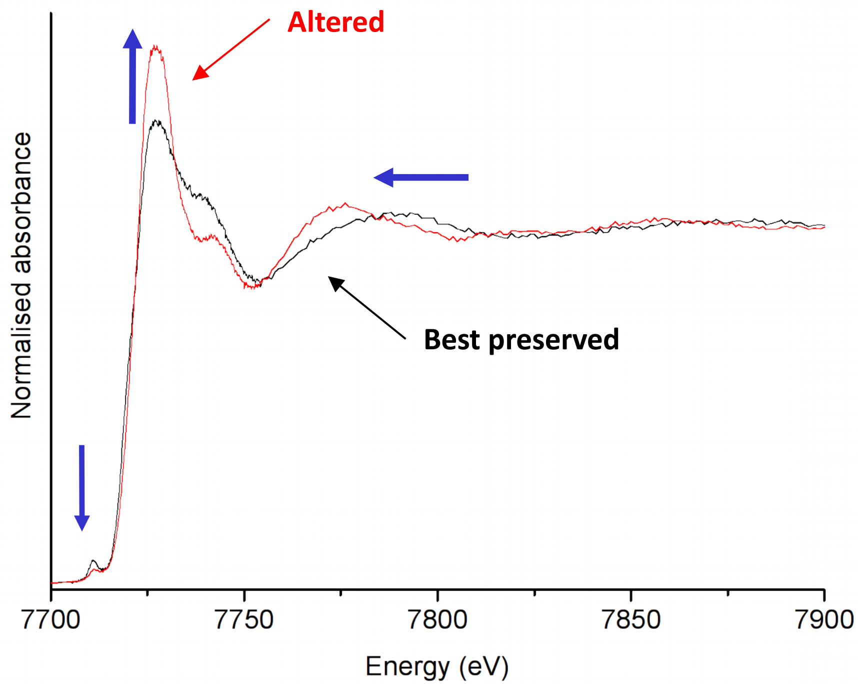
Hypotheses for Smalt degradation:

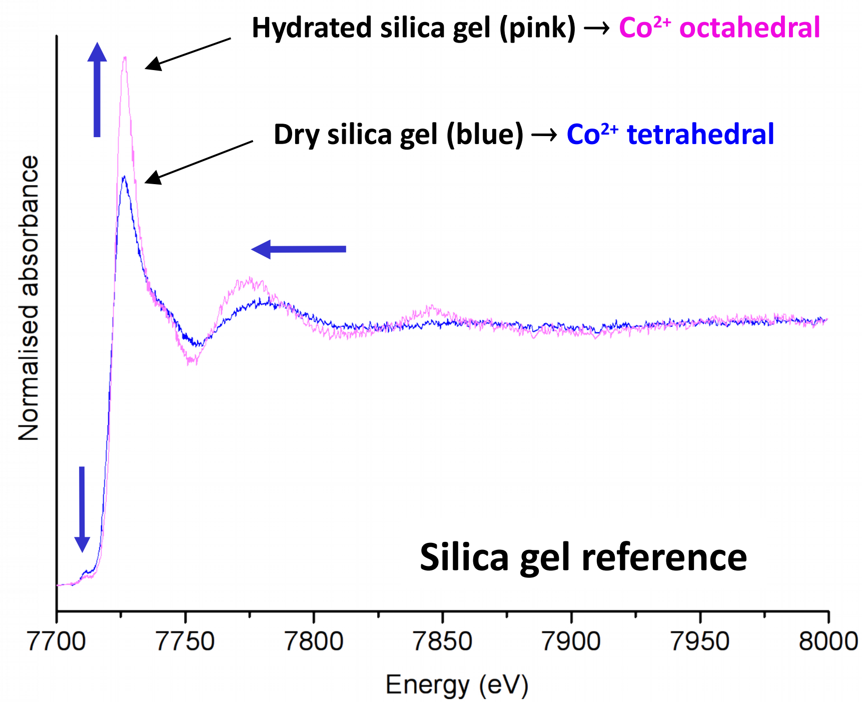
- Cobalt leaching: **No**
- Cobalt speciation: **micro-XANES at Co-edge**
- Potassium/Cobalt ratio: **Potassium leaching**
- Cobalt oxidation state: **No**

Complementary spectroscopy techniques also used to investigate binder (FTIR, Raman)

Results: micro-XAS at Co K-edge

Spectral variation from XANES region

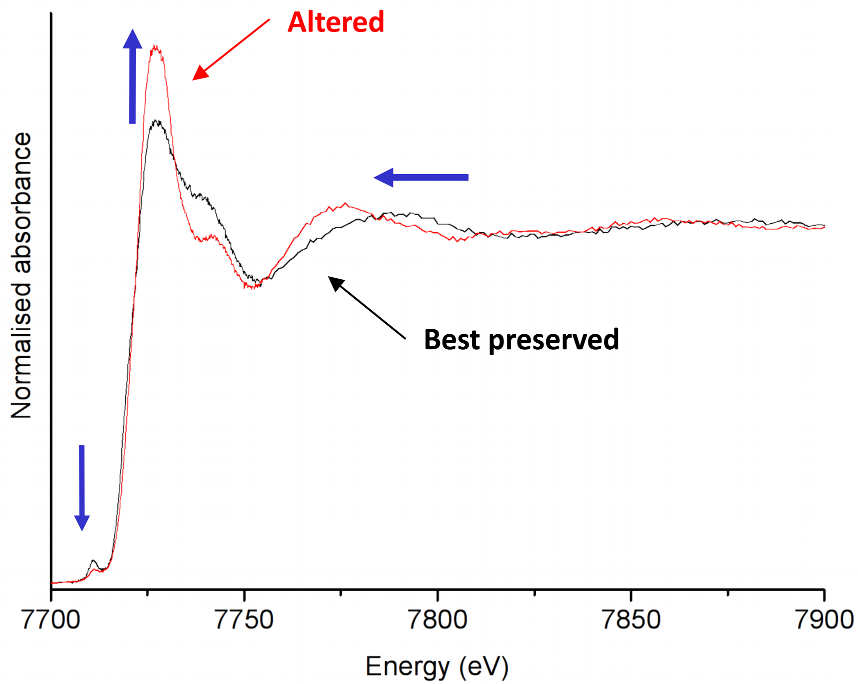




Provided by L. Robinet

Results: micro-XAS at Co K-edge

Spectral variation from XANES region



Co–O distance from EXAFS region

Sample	State	R (Å)	N (dN)
Veronese L2925	Unaltered	1.95	4.4 (2)
	Altered 1	2.03	5.5 (2)
	Altered 2	2.06	6.0 (3)
Murillo NG13S8	Unaltered	1.95	4.7 (2)
	Altered 1	1.97	5.5 (2)
Fiammingo NG5467	Unaltered	1.95	4.9 (1)
	Altered 1	2.00	6.2 (1)
Veronese NG26S6	Unaltered	1.96	4.4 (3)
	Altered 1	2.02	5.6 (1)

➡ Colour change = modification of Co^{2+} environment from mostly tetrahedral towards octahedral coordination

Provided by L. Robinet

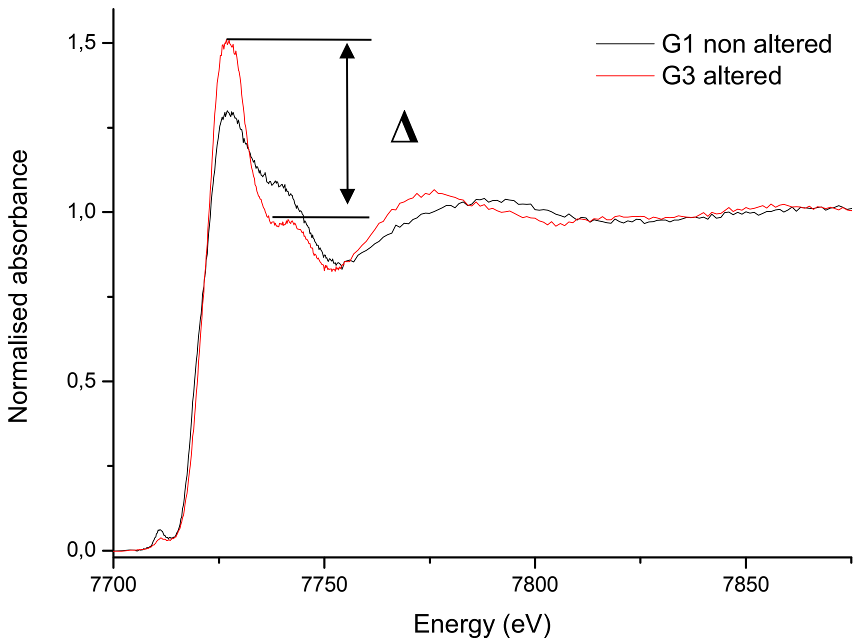
Results

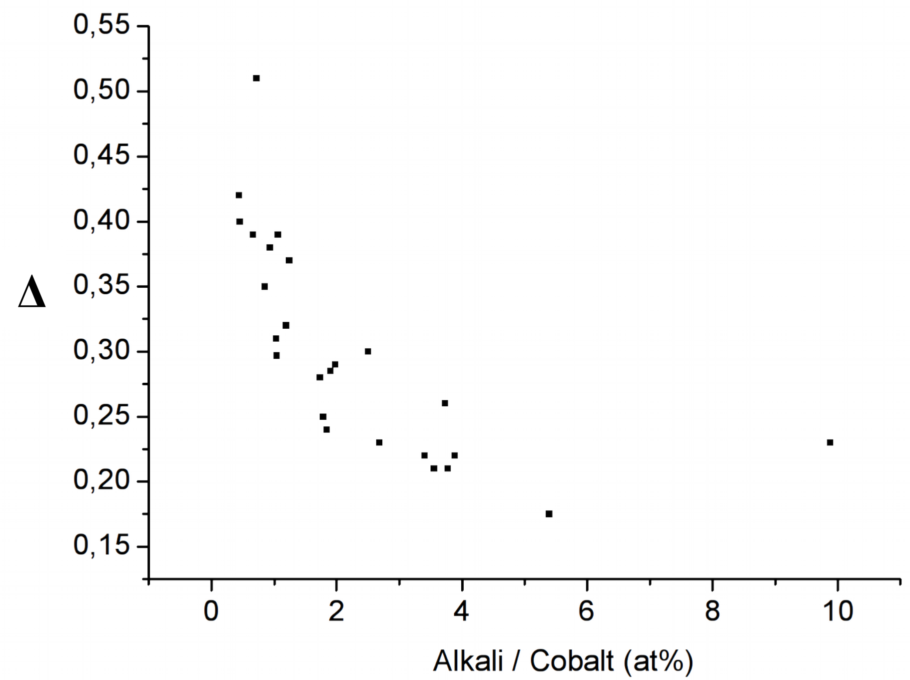
Hypotheses for Smalt degradation:

- Cobalt leaching: **No**
- Cobalt speciation: **Yes**
- Potassium/Cobalt ratio: **Potassium leaching**
- Cobalt oxidation state: **No**

Complementary spectroscopy techniques also used to investigate binder (FTIR, Raman)

Results: Correlation Co speciation / K leaching?





Alkali content affects Co^{2+} coordination

Leaching of alkali responsible of coordination change

Provided by L. Robinet

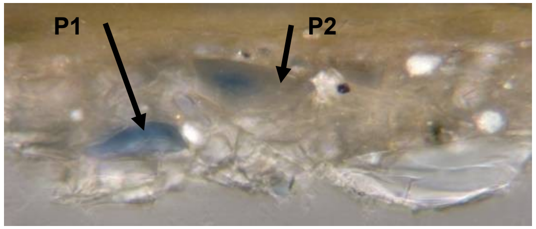
Results: Overview of study

Hypotheses for Smalt degradation:

- Cobalt leaching: **No**
- Cobalt speciation: **Yes**
- Potassium/Cobalt ratio: **Potassium leaching**
- Cobalt oxidation state: **No**

Complementary spectroscopy techniques also used to investigate binder (FTIR, Raman)

Additional study

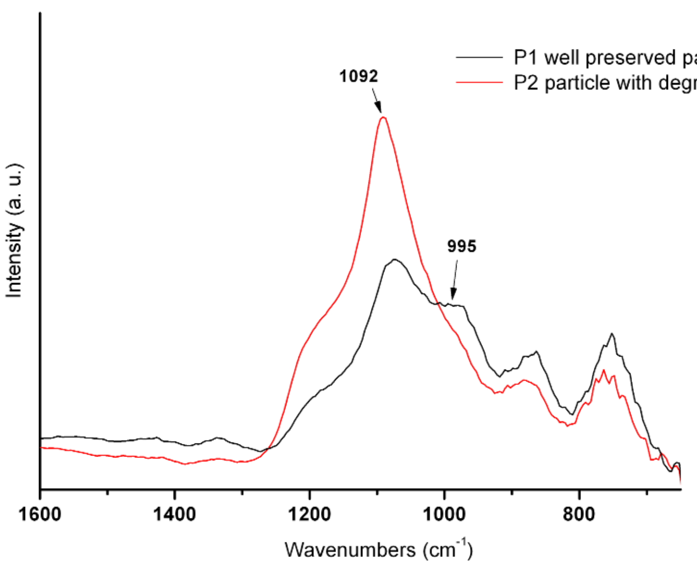


Quantitative SEM-EDX analysis

Wt% norm	Al_2O_3	SiO_2	K_2O	CaO	FeO	CoO	NiO	As_2O_3	PbO
P1 blue	1.0	71.8	12.3	1.7	3.1	2.9	0.6	4.8	1.9
P2 degraded	1.0	82.0	3.4	0.4	2.9	3.6	0.7	3.6	2.3

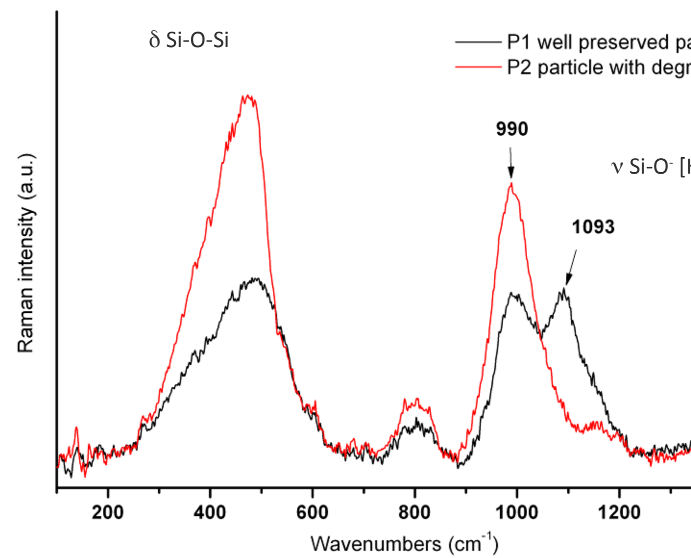
SR reflectance FTIR microspectroscopy SMIS beamline, SOLEIL

- Reflectance mode
- Beam size 11 × 11 µm
- 8 cm^{-1}, 128 scans



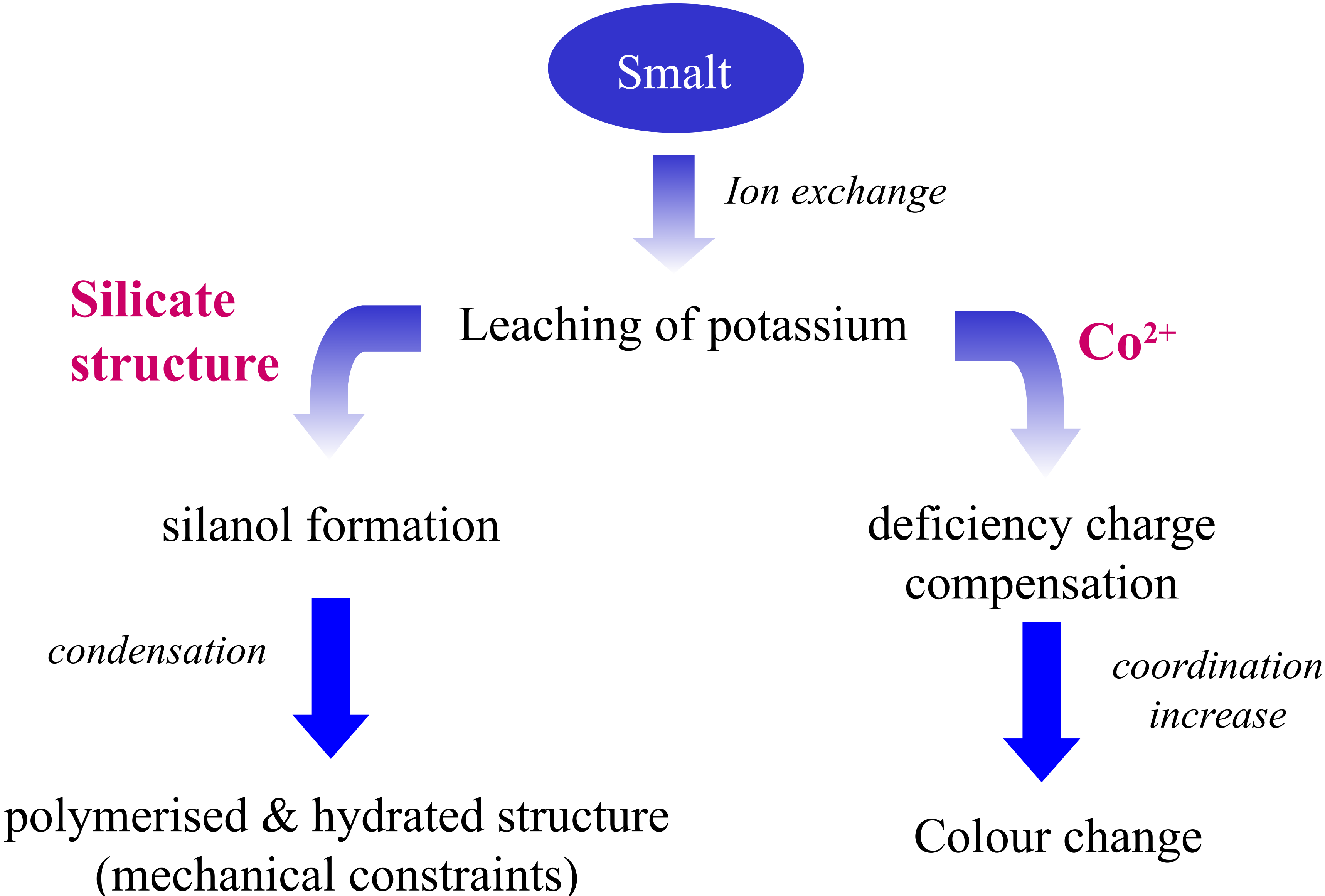
Micro Raman spectroscopy

- Laser 532 nm
- Power: 5 mW
- Beam size 2 µm



Provided by L. Robinet

Proposed mechanism for Smalt discoloration



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