Crystals in ancient and modern glass

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What is the common point?

➢ Historical glass/glazes


Egyptian vase 15th BCE


Roman mosaic


Portland vase
(British Museum, London)


Red stained glasses 13th CE


Limoges enamel 12th CE


Yellow stained glasses 15th CE

➢ Modern products

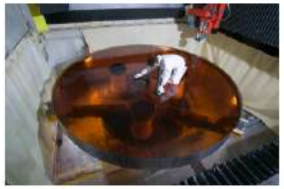

Opal cup 20th CE


Keralite® Kerablack®

→ Cooktop
(Eurokera / Corning-Saint-Gobain)


→ CorningWare "Vision" ™
an historical product


→ biocompatible material


→ telescope mirror
Very Large Telescope (VLT – Eso)
Zerodur® (Schott)

Crystallization is used since Antiquity

Filigrane glass (Venice)
16th century

Filigrane glass (Doremus)
21th century

the use of crystals in glasses has been a common practice for 3500 years:

- to achieve specific colors ⇒ white, yellow, red
- to opacify ⇒ tesserae, glaze, enamel

glass on ceramics

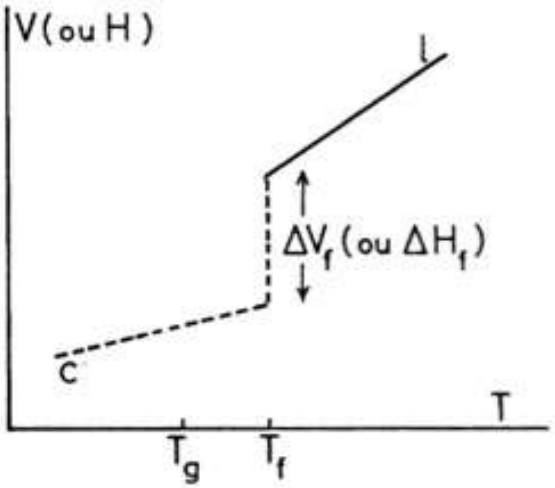
glass on metals

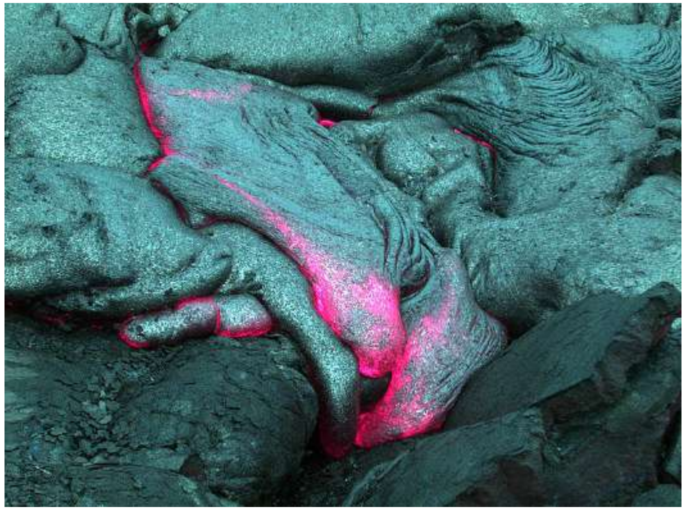
- to achieve new properties (thermal expansion, mechanical) ⇒ modern glass-ceramics

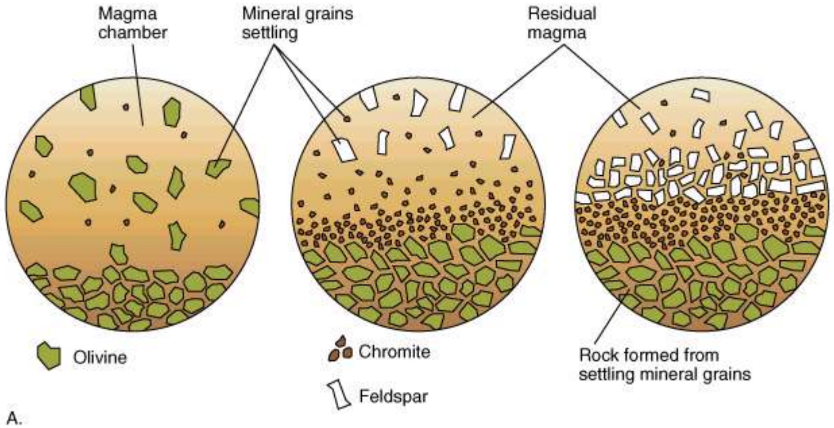
Crystallization from the liquid state

- Crystallization can occur when a liquid is cooling down

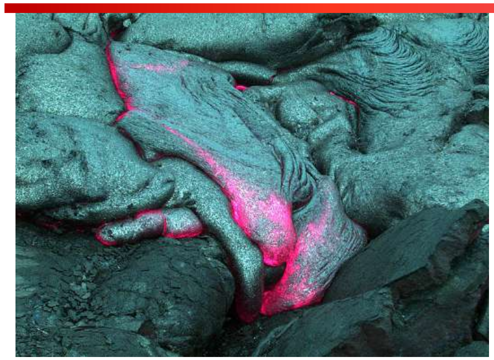
⇒ very important for geological processes

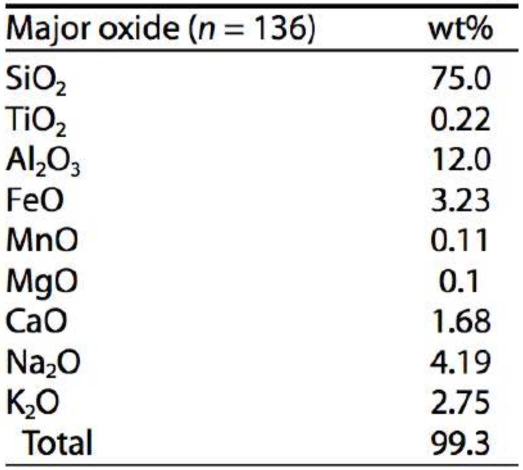




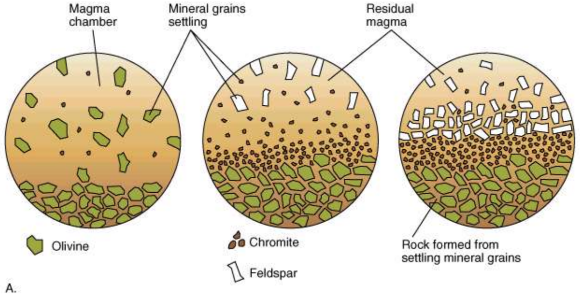


Crystals also in natural volcanic glass, obsidian





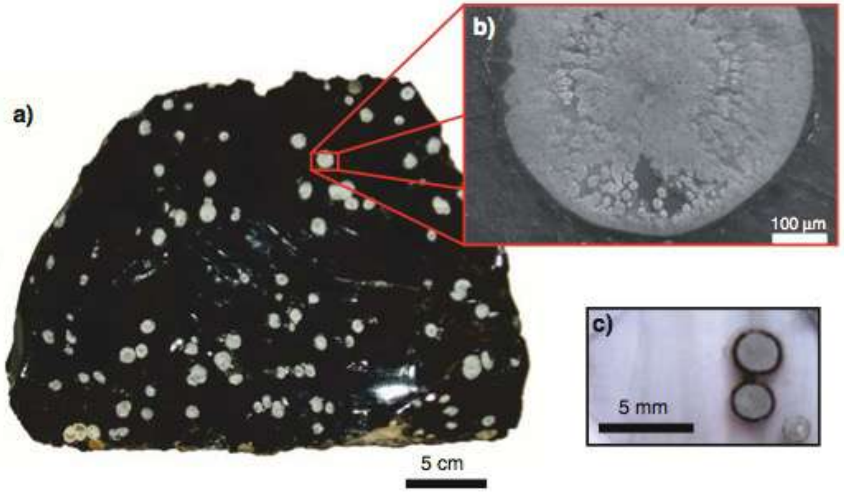
Major oxide ($n = 136$)	wt%
SiO_2	75.0
TiO_2	0.22
Al_2O_3	12.0
FeO	3.23
MnO	0.11
MgO	0.1
CaO	1.68
Na_2O	4.19
K_2O	2.75
Total	99.3



Snowflake obsidian.
Image © iStockphoto /
Fernando Sanchez.

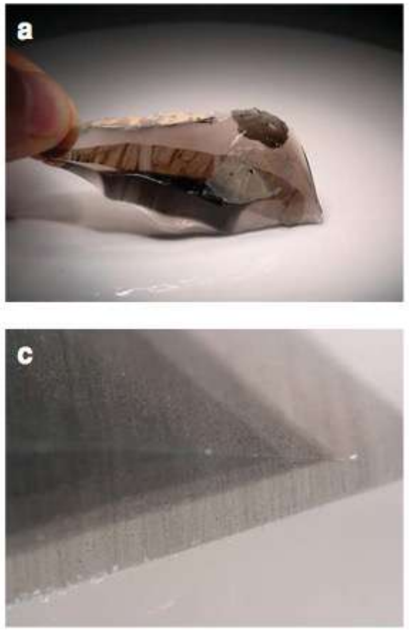
Crystals also in natural volcanic glass, obsidian

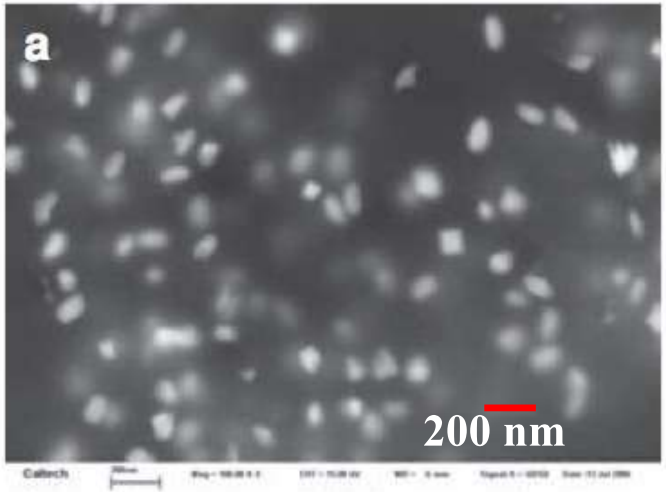
➢ From macro …



•Plagioclase, SiO_2 polymorphs (cristobalite), magnetite (Fe_3O_4)

… to nanoscale





Iron spinel
Magnetite nanocrystals (Fe_3O_4)

Watkins et Rossman, *Can. Mineral.* 2007

Importance of the scale !

Importance of nano-crystals ⇨ color

Obsidian

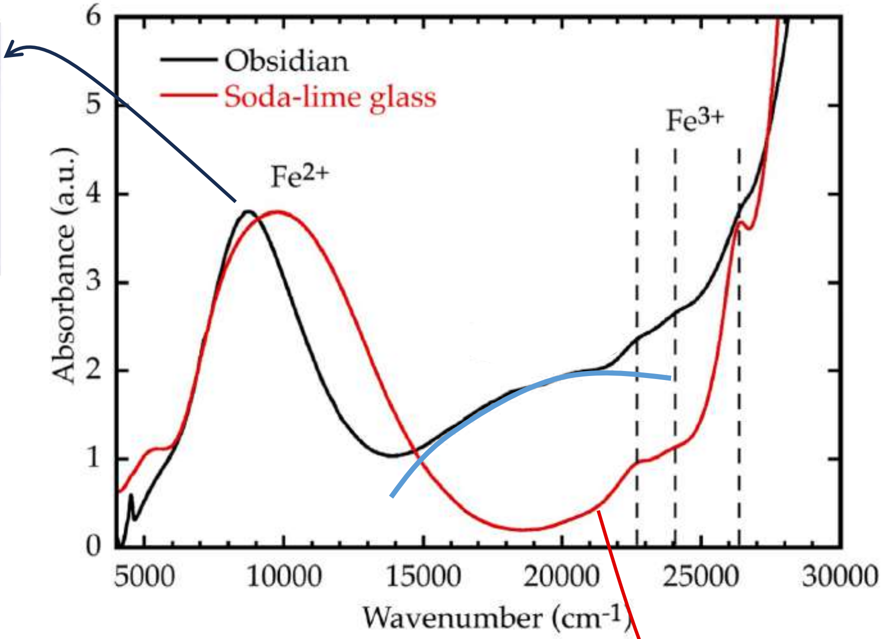
Same iron content

↔

Sodo-calcic glass

Importance of nano-crystals ➪ color

Optical absorption spectroscopy



Distributed Fe^{2+} environments

Fe^{2+} in regular octahedral environment

Metal-Oxygen charge transfer Fe^{3+}-O^{2-}

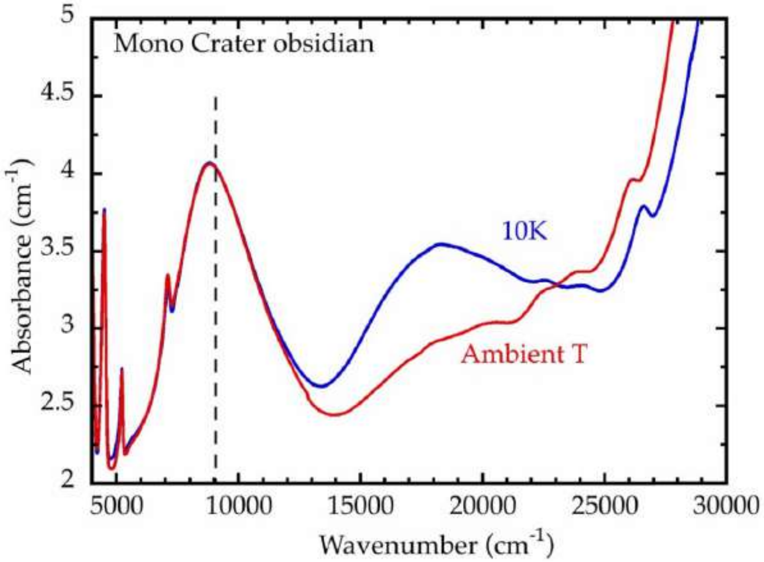
❑ Galoisy & Calas, *Chem. Geol.* 559 (2021) 119925
doi: 10.1016/j.chemgeo.2020.119925
❑ Cormier, Galoisy, Lelong, Calas, *Comptes rendus Physique* 24 (2023) 199
doi: 10.5802/crphys.150

Importance of nano-crystals ⇨ color

Variable temperature optical absorption spectroscopy

IVCT (Inter-valence charge transfer) Fe^{2+}-O-Fe^{3+}

T↘ ⇨ IVCT↗



- ❑ Galoisy & Calas, *Chem. Geol.* 559 (2021) 119925
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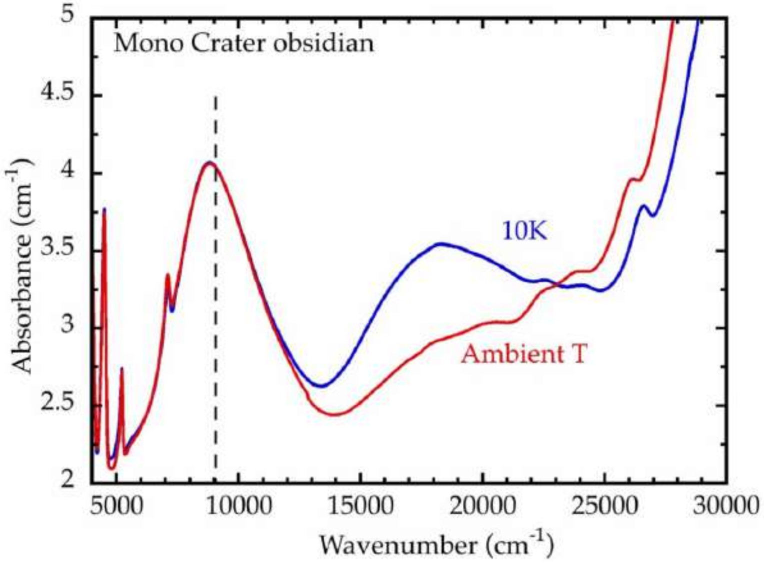
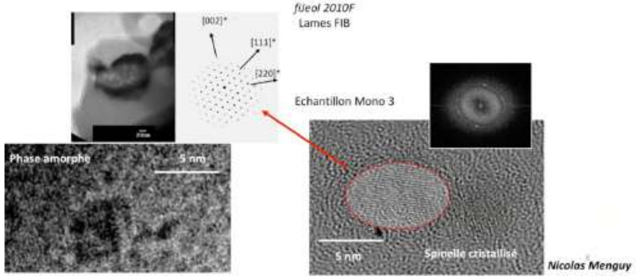


edge-sharing sites ⇒ a Fe-rich local structure already present in the glass

Obsidian contains nanolites iron spinel (~5 nm) and iron-rich amorphous regions



Iron rich clusters/nanolites confirm by EPR

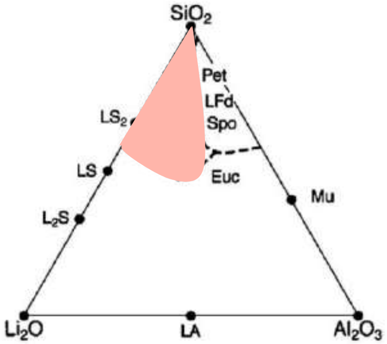
poster Dimitrios Isaias

- ❑ Galoisy & Calas, *Chem. Geol.* 559 (2021) 119925
doi: 10.1016/j.chemgeo.2020.119925
- ❑ Cormier, Galoisy, Lelong, Calas, *Comptes rendus Physique* 24 (2023) 199
doi: 10.5802/crphys.150

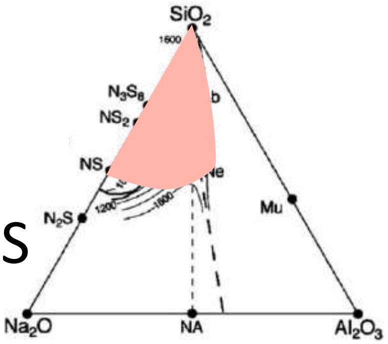
Aluminosilicate systems

- ➢ monovalent cations

LAS

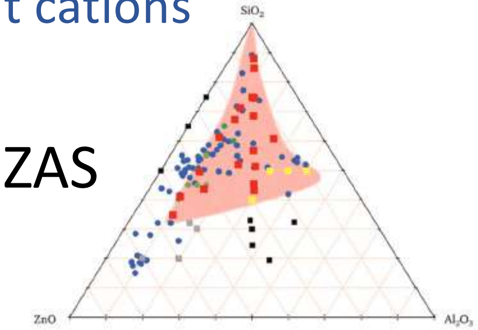


NAS

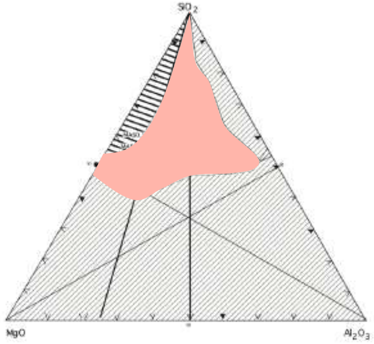


- ➢ divalent cations

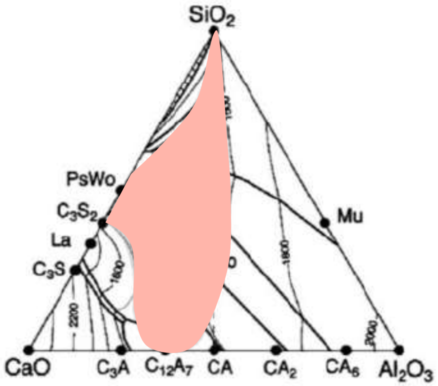
ZAS



MAS



CAS



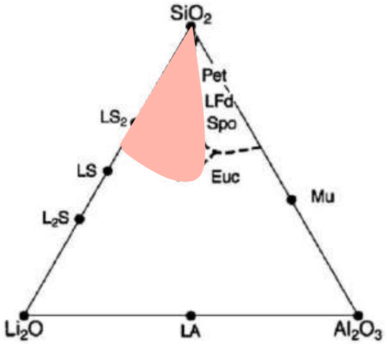
- Glass domain similar for the ZAS and MAS system
- Likely a similar structural role for Zn^{2+} and Mg^{2+}

- ❑ Neuville, Cormier, Massiot, *Chem. Geol.* 229 (2006) 173 doi: 10.1016/j.chemgeo.2006.01.019
- ❑ Guignard & Cormier, Chem. Geol. 256 (2008) 111 doi: 0.1016/j.chemgeo.2008.06.008
- ❑ Neuville, Cormier, Montouillout, Florian, Millot, Rifflet, Massiot, *Am. Miner.* 93 (2008) 1721 doi: 10.2138/am.2008.2867
- ❑ Cormier, Delbes, Baptiste, Montouillout, *J. Non-Cryst. Solids* 555 (2021) 120609 doi: 10.1016/j.jnoncrysol.2020.120609

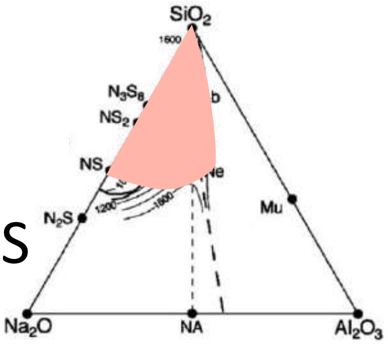
Al environments, ^{27}Al NMR

- ➢ monovalent cations

LAS



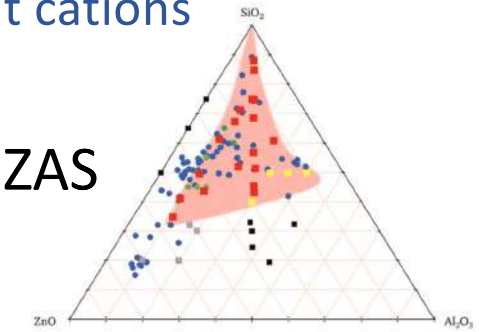
NAS



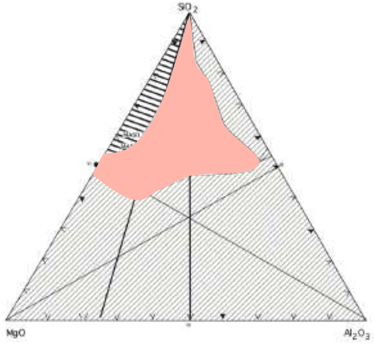
- only $^{[4]}$Al

- ➢ divalent cations

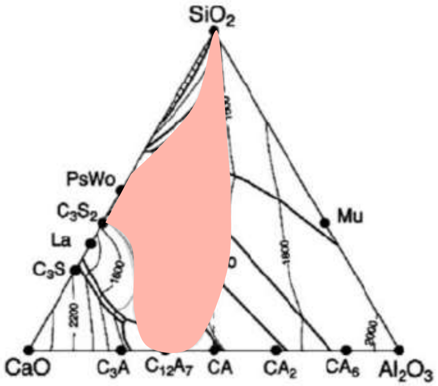
ZAS



MAS



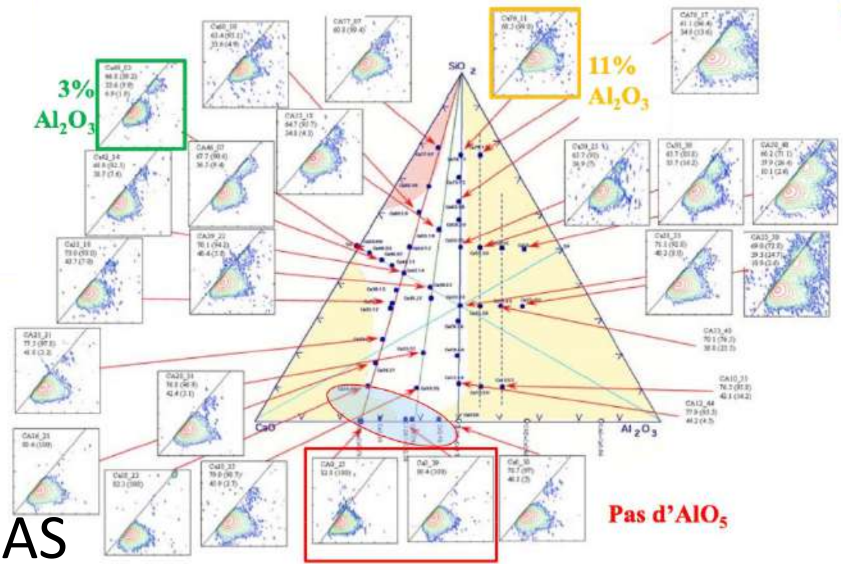
CAS



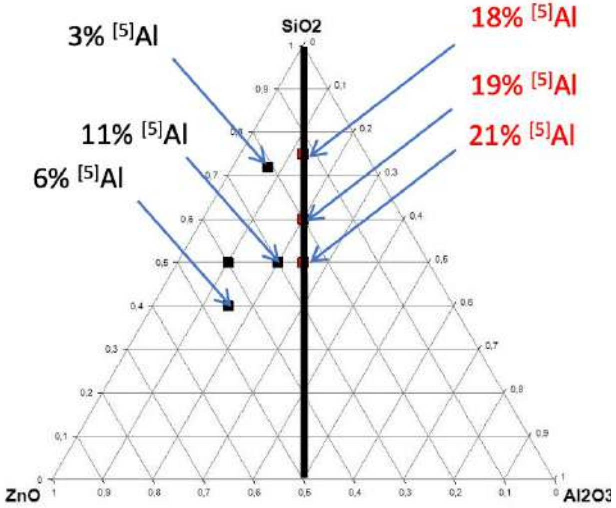
- Al improves glass forming ability
- $^{[5]}$Al highest proportion along the tectosilicate

- ❑ Neuville, Cormier, Massiot, *Chem. Geol.* 229 (2006) 173 doi: 10.1016/j.chemgeo.2006.01.019
- ❑ Guignard & Cormier, Chem. Geol. 256 (2008) 111 doi: 0.1016/j.chemgeo.2008.06.008
- ❑ Neuville, Cormier, Montouillout, Florian, Millot, Rifflet, Massiot, *Am. Miner.* 93 (2008) 1721 doi: 10.2138/am.2008.2867
- ❑ Cormier, Delbes, Baptiste, Montouillout, *J. Non-Cryst. Solids* 555 (2021) 120609 doi: 10.1016/j.jnoncrysol.2020.120609

Al coordination in aluminosilicate glasses



CAS



3% $^{[5]}Al$

11% $^{[5]}Al$

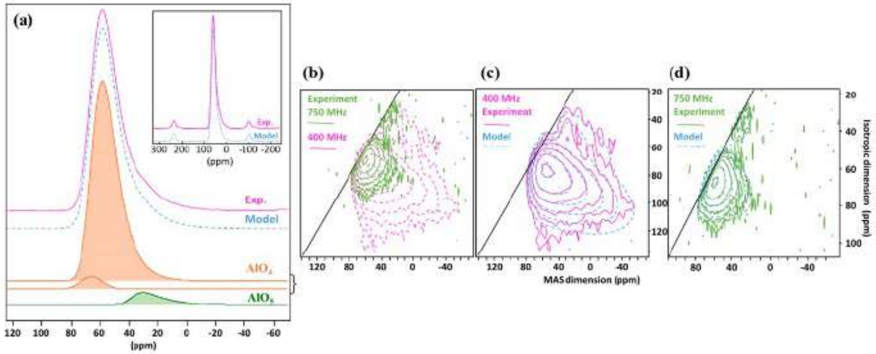
6% $^{[5]}Al$

18% $^{[5]}Al$

19% $^{[5]}Al$

21% $^{[5]}Al$

ZAS



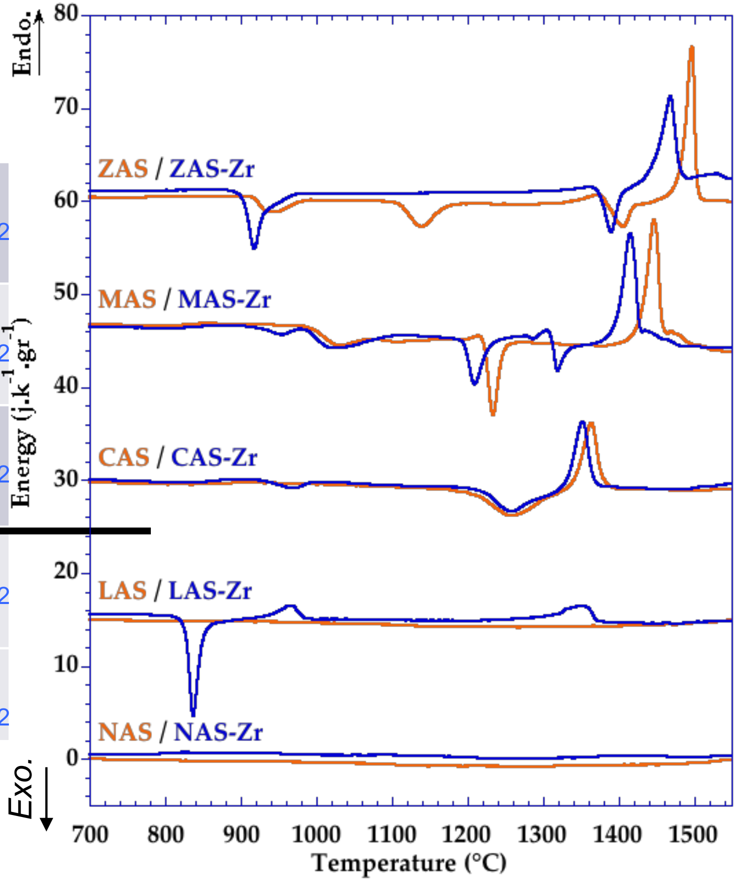
- Presence of $^{[5]}Al$ in the left part of the diagram
- High proportions of $^{[5]}Al$ on the tectosilicate join

Different glasses – different nucleation behaviors

Setaram Multi-HTC 96, under N2 flux

ZnAS-Zr	1ZnO-1,21Al_2O_3-6,8 SiO_2	4$\%_{wt}$ ZrO_2
MgAS-Zr	1MgO-1,21Al_2O_3-6,8 SiO_2	4$\%_{wt}$ ZrO_2
CaAS-Zr	1CaO-1,21Al_2O_3-6,8 SiO_2	4$\%_{wt}$ ZrO_2
LiAS-Zr	1Li_2O-1,21Al_2O_3-6,8 SiO_2	4$\%_{wt}$ ZrO_2
NaAS-Zr	1Na_2O-1,21Al_2O_3-6,8 SiO_2	4$\%_{wt}$ ZrO_2

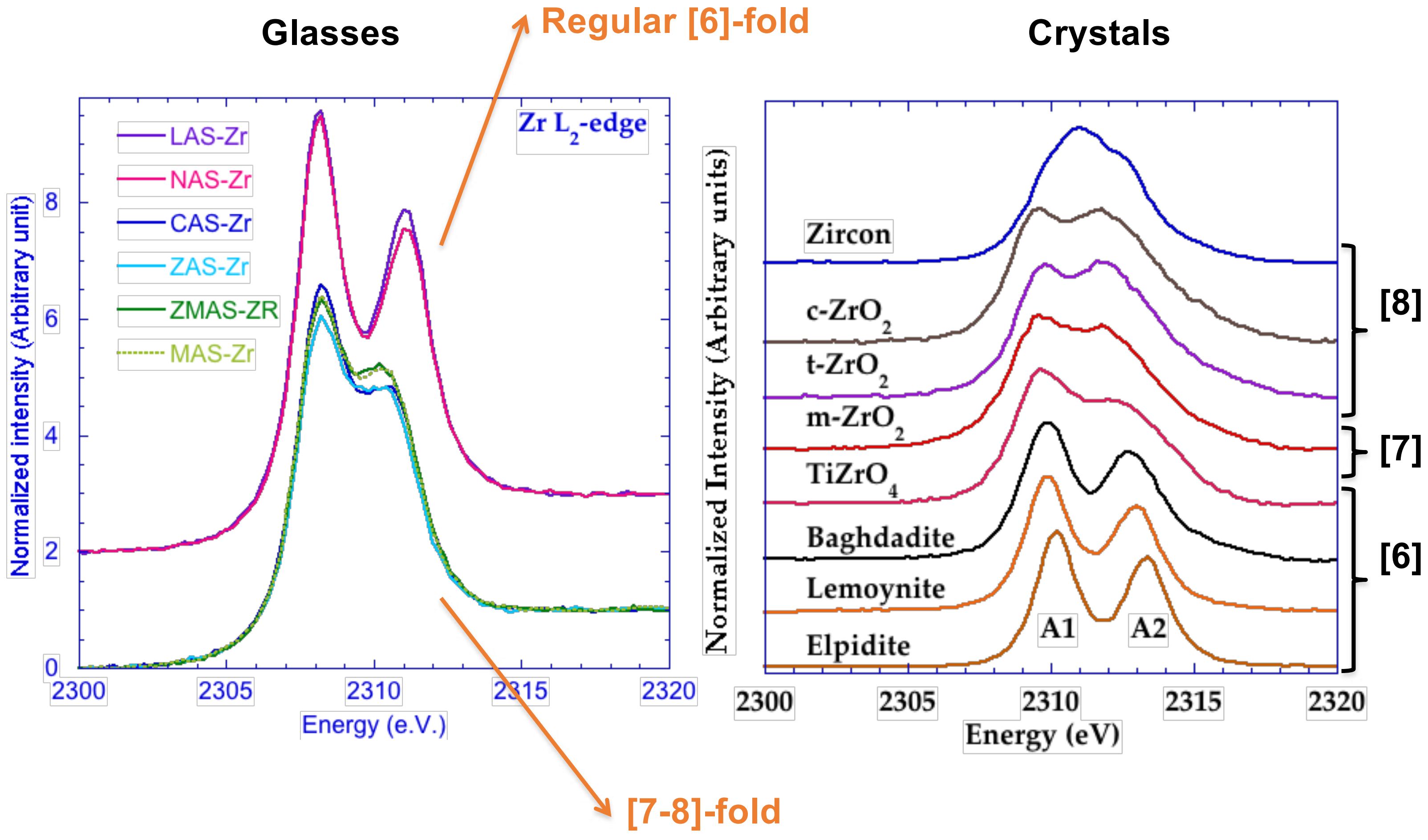
DSC 5 $K.min^{-1}$



Role of Zr^{4+} in those matrices: Comparison of Zr^{4+} bearing and Zr^{4+} free parent-glasses

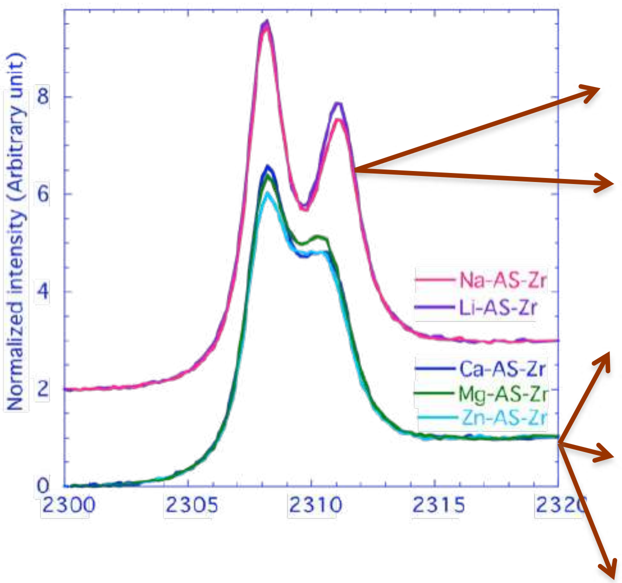
- Cormier at al., *Mater. Chem. Phys.* 152 (2015) 41
doi: 10.1016/j.matchemphys.2014.12.008

Is there a specific Zr site for nucleation ?



Is there a specific Zr site for nucleation ?

Zr $L_{2,3}$-edge XANES LUCIA (SOLEIL)



Na-AS-Zr
No nucleation effect

Li-AS-Zr
Strong nucleation effect

Ca-AS-Zr
Weak nucleation effect

Mg-AS-Zr
Nucleation effect

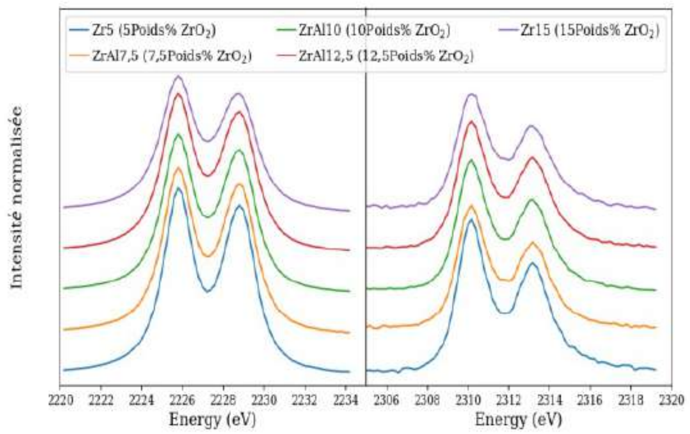
Zn-AS-Zr
Strong nucleation effect

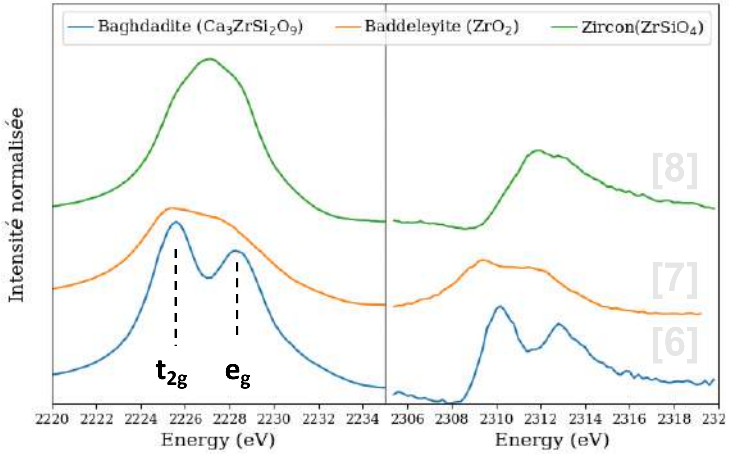
➔ No link between coordination and nucleation effect

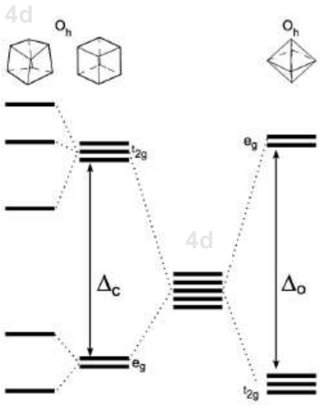
Is there a specific Zr site for nucleation ?

Verre Na_2O-CaO-SiO_2-Al_2O_3 + ZrO_2
de 5 à 15 poids%

Comparaison références cristallines







Seuils $L_{2,3}$ de Zr

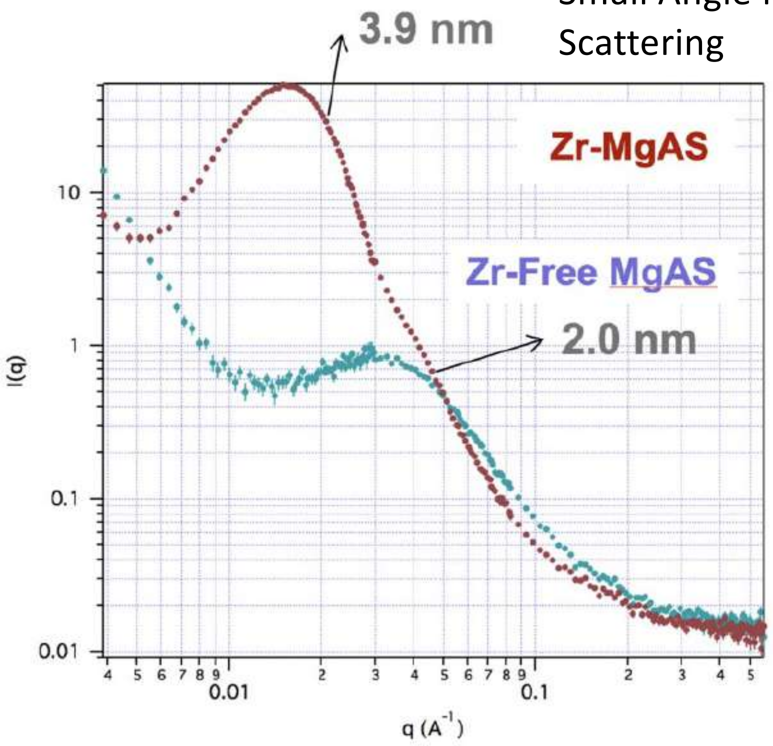
Pas de changement de coordinence de Zr avec la concentration

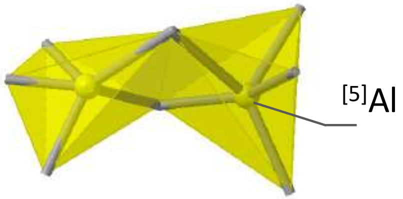
❑ Ficheux at al., *J. Non-Cryst. Solids* 539 (2020) 120050
doi: 10.1016/j.jnoncrysol.2020.120050

Thèse Maxime Ficheux
Coll. SVI-Saint Gobain Recherche

Heterogeneities in aluminosilicate glasses

Small Angle Neutron Scattering



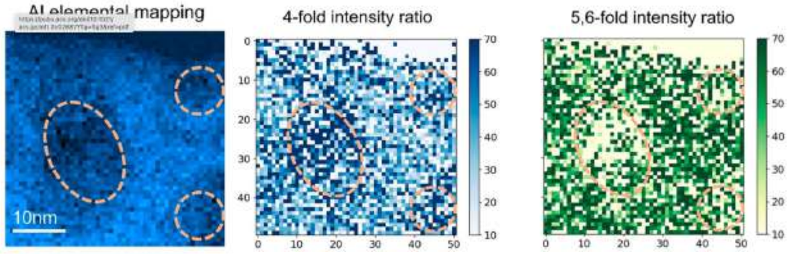


AlO_5 and AlO_6 polyhedra

$\Rightarrow$ important edge-sharing linkages

$\Rightarrow$ denser regions formed by $^{[5]}$Al–$^{[6]}$Al-rich domains

$50SiO_2$-$50Al_2O_3$ glass

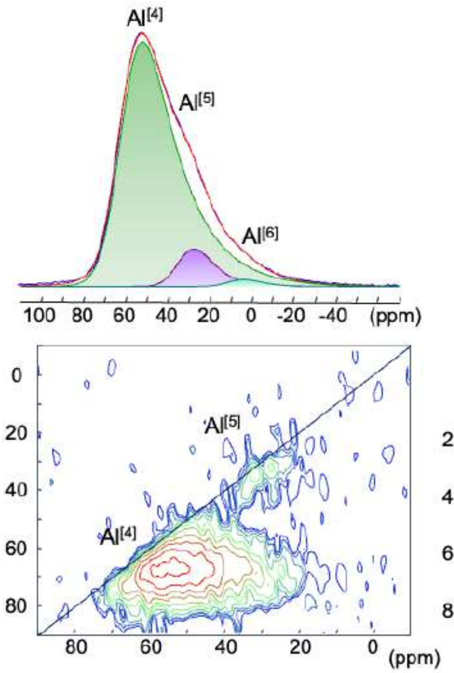


❑ Cormier, Galoisy, Lelong, Calas, *Comptes rendus Physique* 24 (2023) 199
doi: 10.5802/crphys.150

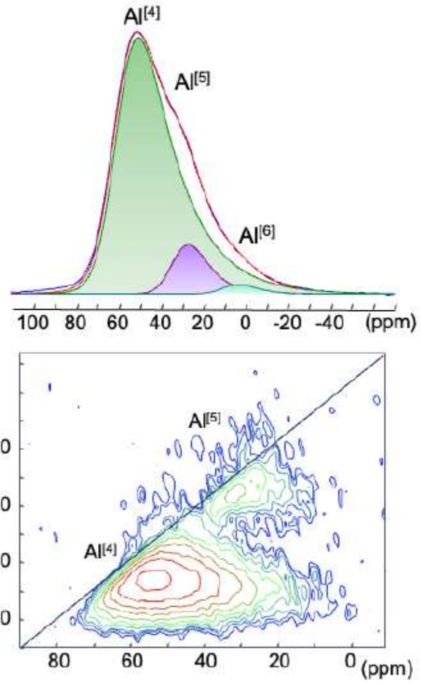
❑ Liao et al., *Phys. Chem. Lett.* 11 (2020) 9637
doi: 10.1021/acs.jpclett.0c02687

Heterogeneities in aluminosilicate glasses with Zr

MAS without Zr



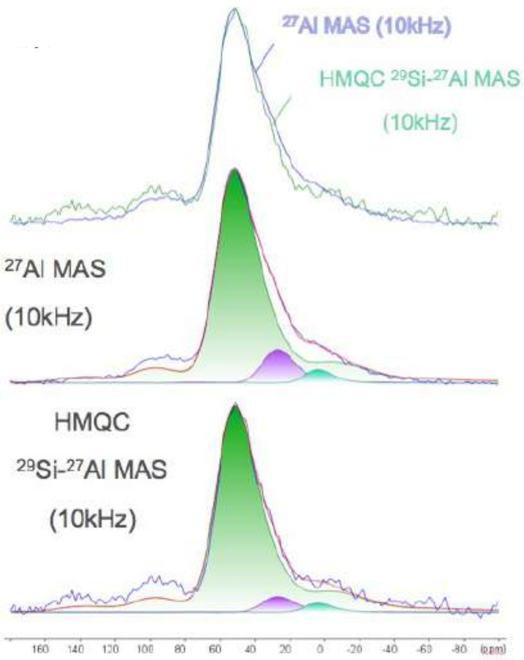
MAS with Zr



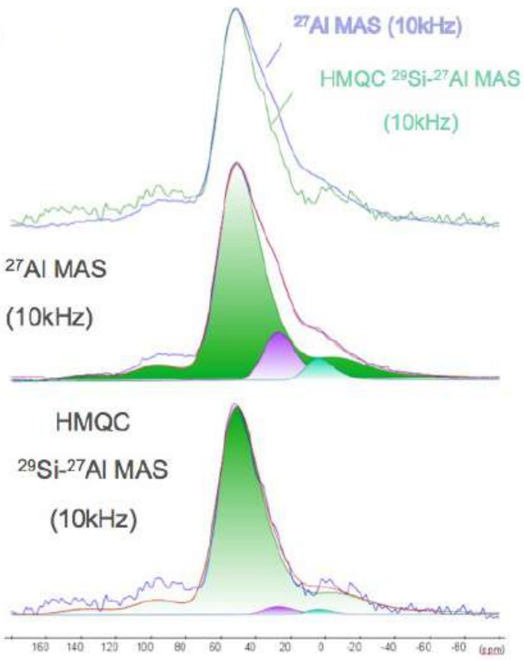
AlO_5 and AlO_6 proportions increase as ZrO_2 is added

Connectivity between Al and Si

MAS without Zr



MAS with Zr



^{29}Si-^{27}Al heteronuclear correlation (HMQC)

aluminum connected to at least one silicon

✓ Si atoms are more associated with $^{[4]}$Al than with $^{[5]}$Al or $^{[6]}$Al

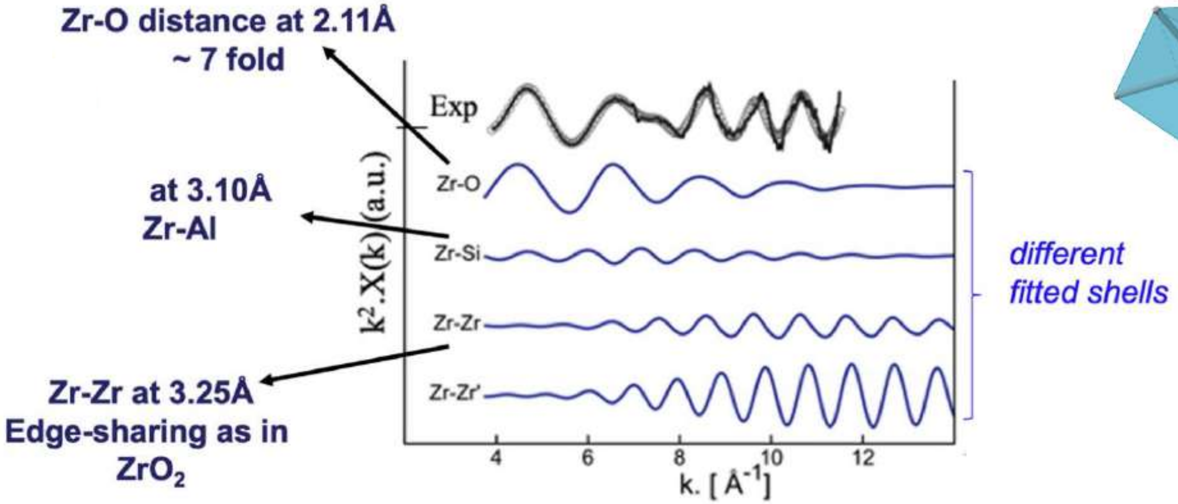
⇨ Si-rich regions having a strong connectivity with $^{[4]}$Al

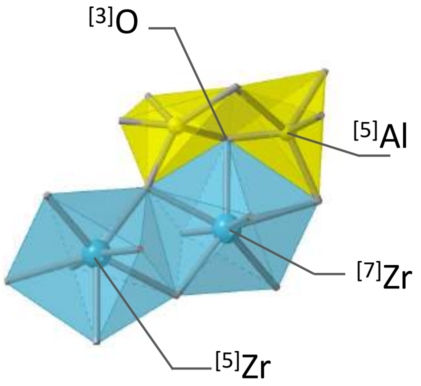
✓ almost no $^{[5]}$Al and $^{[6]}$Al are distinguishable with Zr

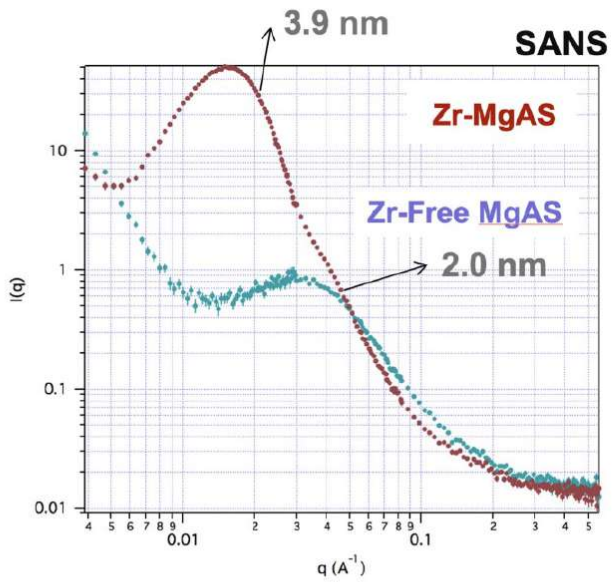
⇨ $^{[5]}$Al and $^{[6]}$Al have a preference to be localized in regions where Si content is poor

Heterogeneities in aluminosilicate glasses with Zr

Glass $MgO\text{-}Al_2O_3\text{-}SiO_2\text{-}ZrO_2$
Zr K-edge EXAFS







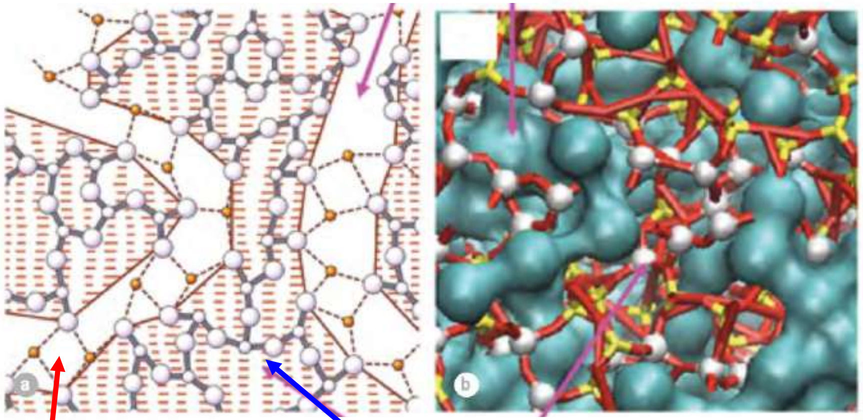
- ❑ Dargaud et al., *J. Non-Cryst. Solids* 356 (2010) 2928
doi: 10.1016/j.jnoncrysol.2010.05.104
- ❑ Cormier, Galoisy, Lelong, Calas, *Comptes rendus Physique* 24 (2023) 199
doi: 10.5802/crphys.150

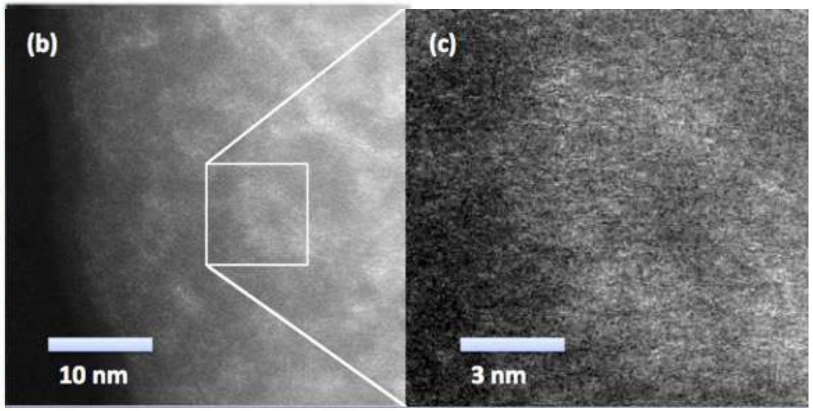
Heterogeneities in aluminosilicate glasses

Glass $MgO-Al_2O_3-SiO_2-ZrO_2$

Electron microscopy in HAADF mode ➪ chemical information

Greaves's model





Zones enriched in network formers

Zones enriched in non-network formers

White zone = regions enriched in **Zr**
➪ non-homogeneous distribution of Zr within the glass structure

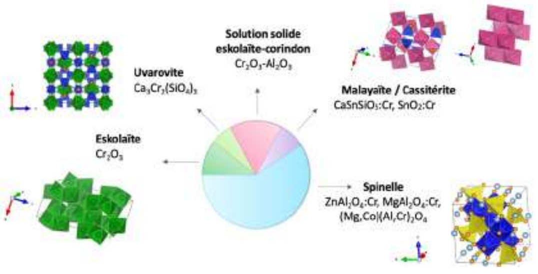
- Dargaud et al. *J. Appl. Phys.* 99 (2011) 21904 doi: 10.1063/1.3610557]
- Cormier & Neuville, *Reflets de la Physique* 74 (2022) 22 doi: 10.1051/refdp/202274022

Crystals in historical glass/glazes

➔ Crystals in glazes

Chromium pigments in glaze decoration of Sèvres's porcelains

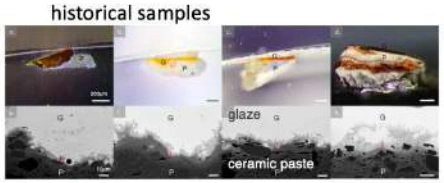
+ reactivity of the pigments in the glaze (L. Verger)



Glazes ceramics objects from Elam (Iran), 1500-539 BCE (A. Aarab, 2023)

➔ Crystals at the paste/glaze interface

M. Godet, T. Roisine, D. Caurant, A. Bouquillon, O. Majérus

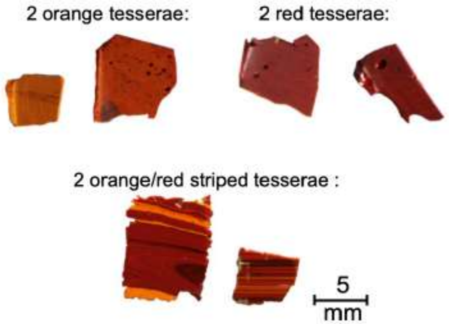


➔ Crystals in Roman glass tesserae

C. Noirot, L. Gardie, N. Schibille

Red and orange coloration

The Roman villa at
Noheda, Cuenca, Spain



Cu^{2+}-Cu^{+} dans les verres

Atmosphère très réductrice : Cu^{+} ion (ne produit aucune couleur) jusqu'à C allique)

- nanoparticules métalliques (cuivre précipité Cu^{0})

⇨ rouge

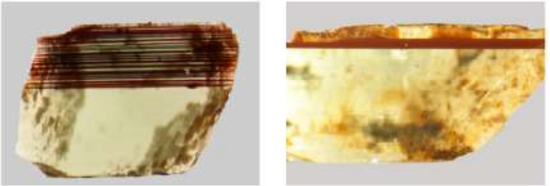
- Cristaux Cu_2O

Coloration + opacification

⇨ rouge ou orange

poster Elise Lanagagne
Cécile Bretonnet

Vitrail de l'Ascension
1120 CE



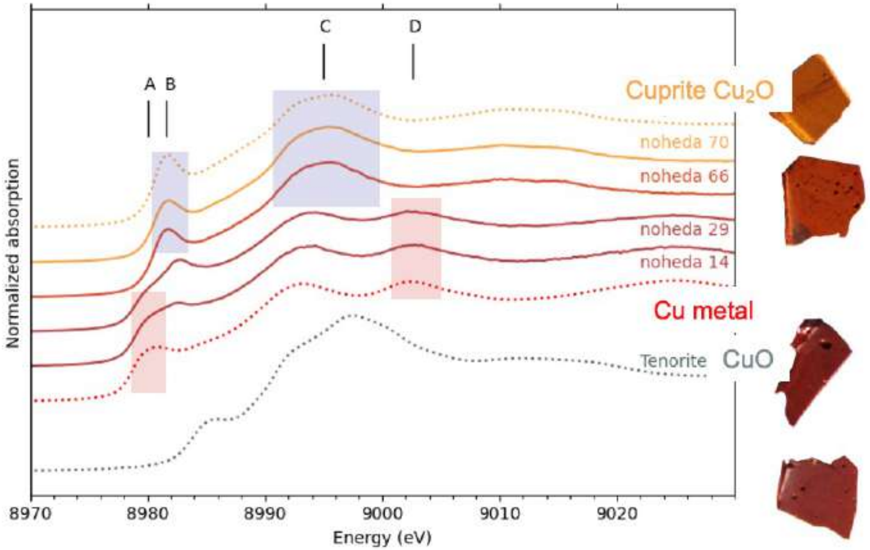
Kunicki-Goldfinger et al. (2014)

Cathédrale du Mans

Monochrome tesserae: origin of the color

SOLEIL SYNCHROTRON

XANES at Cu K-edge
SAMBA beamline



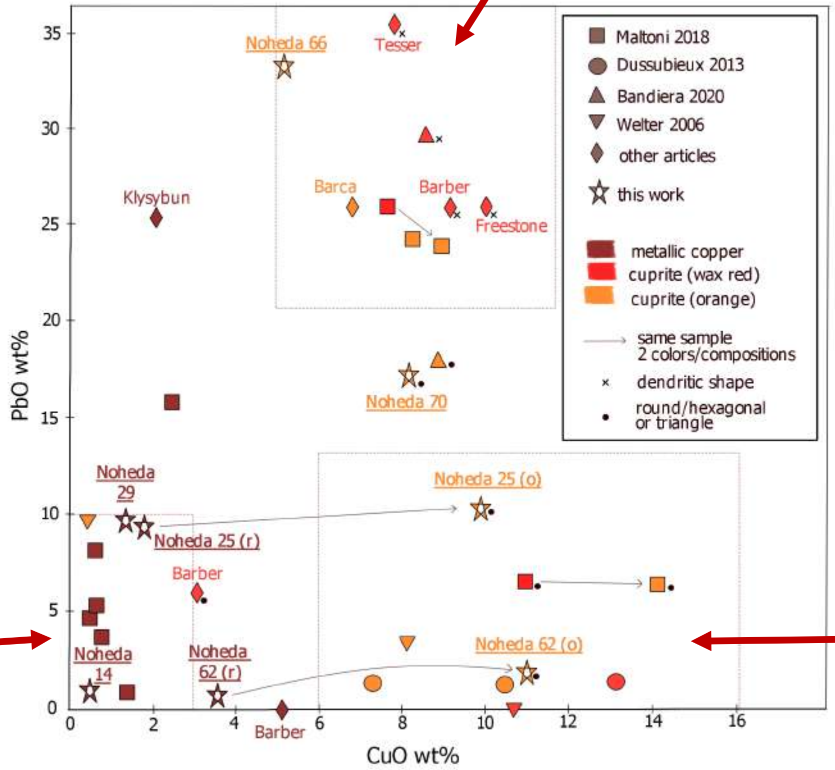
orange : precipitation of crystals of cuprous oxide (Cu_2O)

opaque red : particles of metallic copper

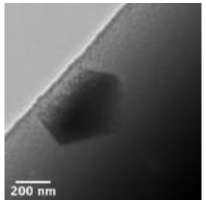
- Noirot at al., *Heritage* 5 (2022) 2628
doi: 10.3390/heritage5030137

Classification: copper vs lead

coloration by Cu_2O
often dendritic, large crystals



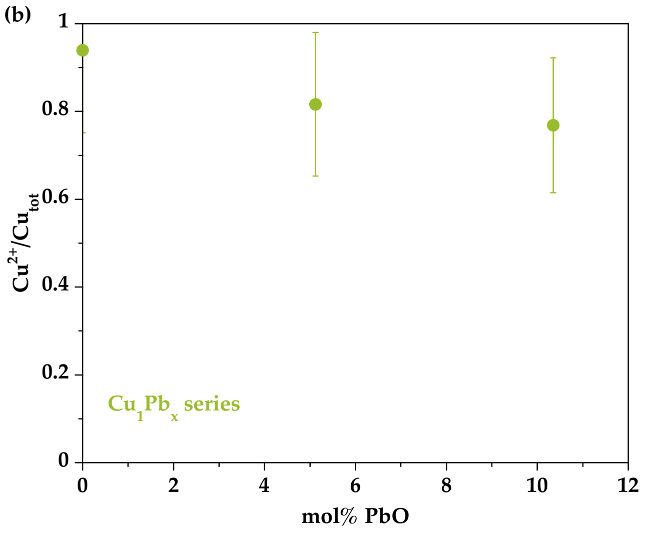
coloration by Cu^0



coloration by Cu_2O
spherical, small crystals

❑ Noirot at al., *Heritage* 5 (2022) 2628
doi: 10.3390/heritage5030137

Role of lead ?



Redox of Cu determined by EPR

Presence of lead changes minimally the Cu redox state

Lead is acting of the viscosity to allow the grwoth of Cu_2O crystals before the crystallization of the remaining silicate glass

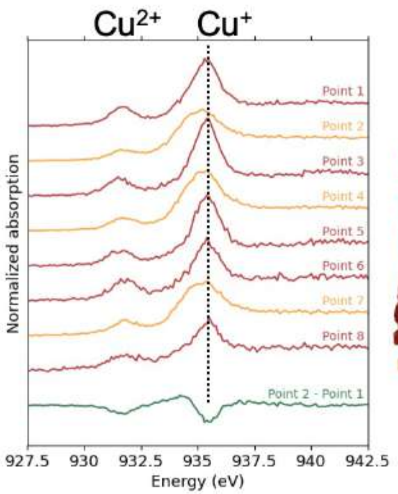
➔ Impact of Pb on Cu_2O shape and color?

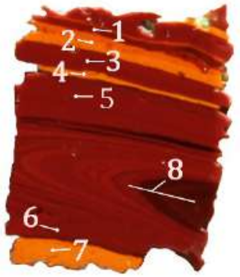
❑ Noirot at al., *submitted*

Striped orange/red tesserae: Cu speciation

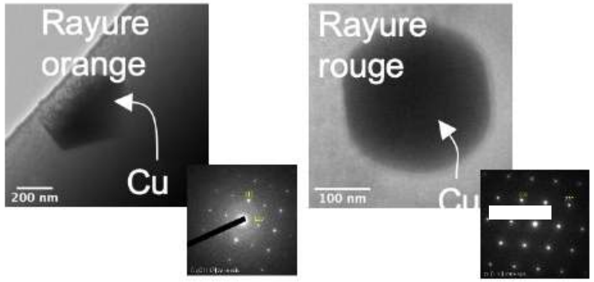
SOLEIL SYNCHROTRON

XANES at Cu L-edge
LUCIA beamline





MET images on FIB blades and electronic diffraction



Orange stripes colored by Cu_2O

Red stripes colored by Cu^0

Cu^{2+} and Cu^{+} present

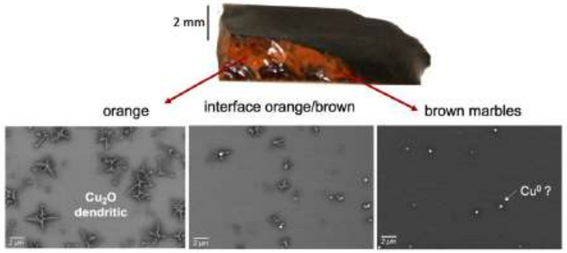
- Same base glass composition.

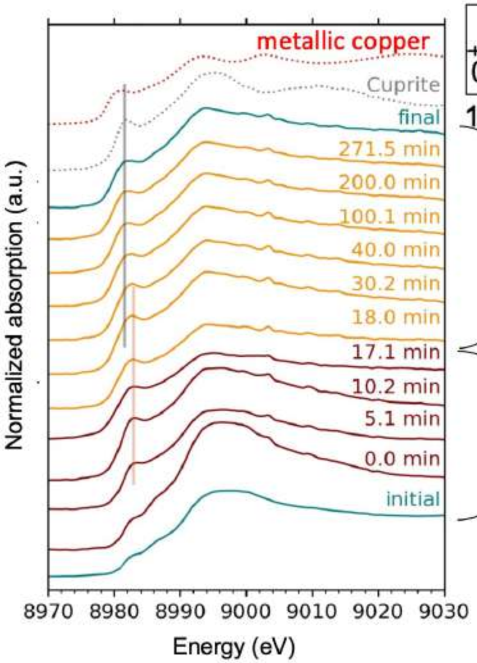
Probably red and orange prepared separately and mixed together in reduced atmosphere

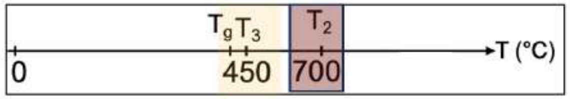
❑ Noirot at al., *Heritage* 5 (2022) 2628
doi: 10.3390/heritage5030137

Reproduction

Influence of temperature on redox control: Study of liquid under Ar/H2







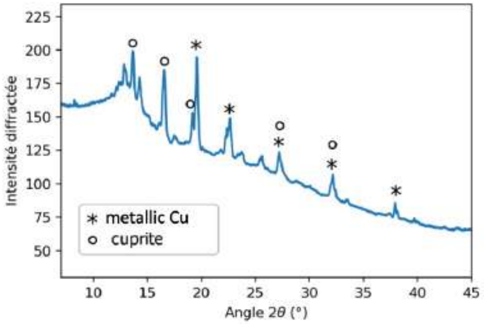
10 % PbO – 15 % CuO

450°C
crystallization

700°C
reduction $Cu^{2+} \rightarrow Cu^{+}$
No crystallization of Cu^0

- **importance of temperature : reduction**
- **annealing allows crystallization (Cu_2O et Cu^0)**

XRD final glass



Cu_2O and metallic Cu
crystallize together

❑ Noirot at al., *Submitted*

- Control of the redox in glasses => composition, oxygen fugacity, temperature
- Ce, Sb, Sn, Fe, Cu

Merci