APPLICATION OF DIFFUSION MODEL TO THE GLASS MELT AND REFRACTORIES INTERACTION AT HIGH TEMPERATURE.

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CEMHTI, Université d'Orléans, Orléans, france

REFRACTORY AND GLASS INTERACTION

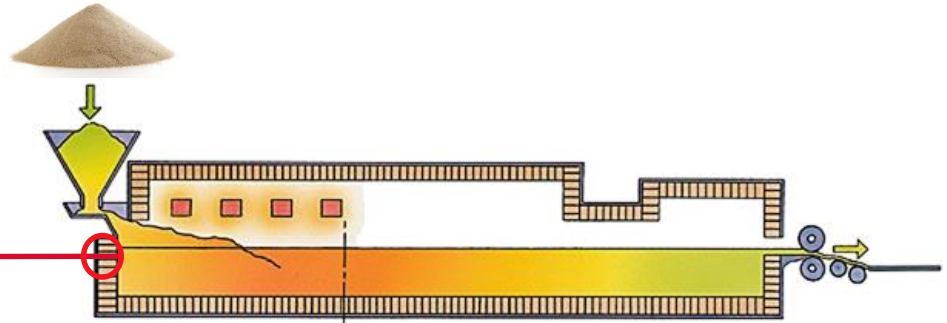
1500°C

ZrO_2 30 à 95 Wt%

ZrO_2 0 Wt%

Refractory

Glass

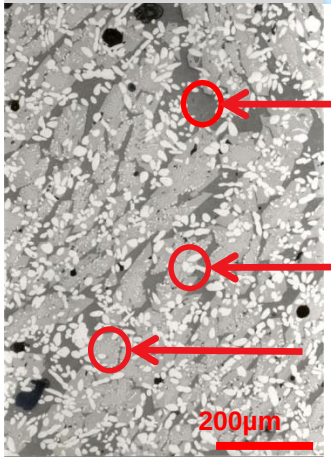


Interaction phenomena:

-Bubbling

-Convection

-Diffusion



Amorphous phase

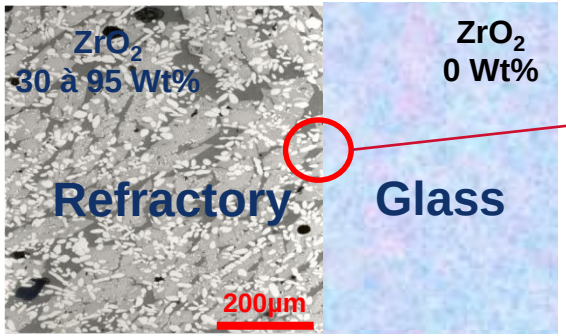
Zirconia

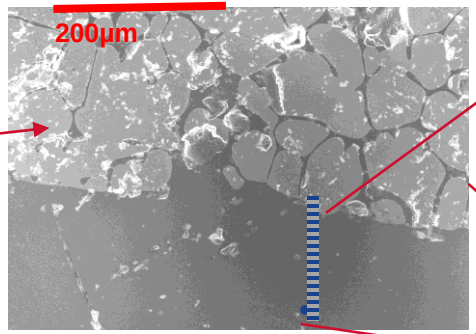
Eutectics Al_2O_3/ZrO_2

REFRACTORY/GLASS DIFFUSION

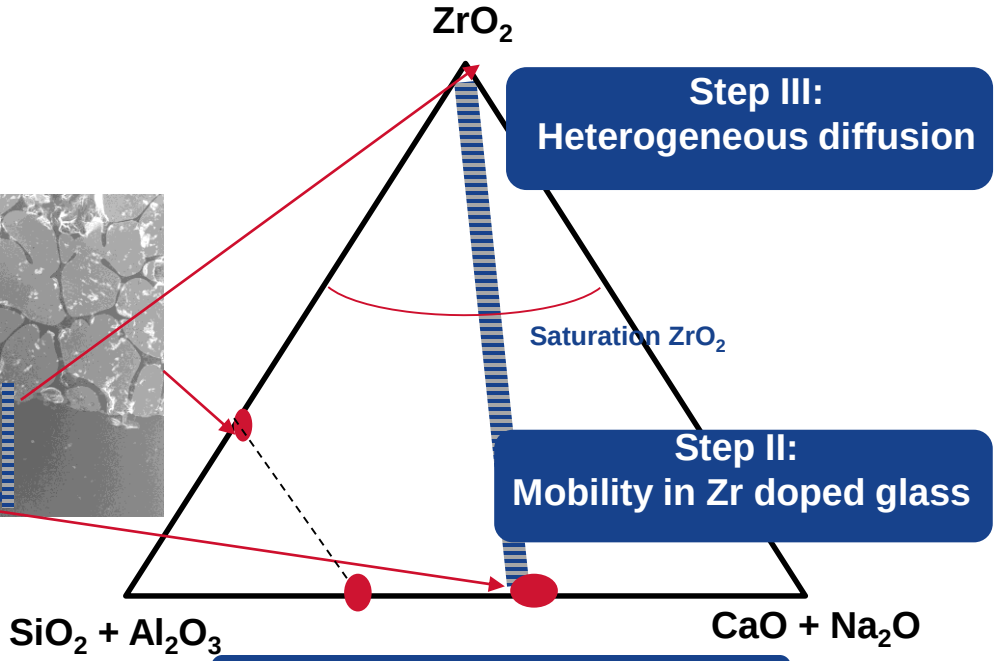
Complex microscopic process: (µm scale)

1500°C





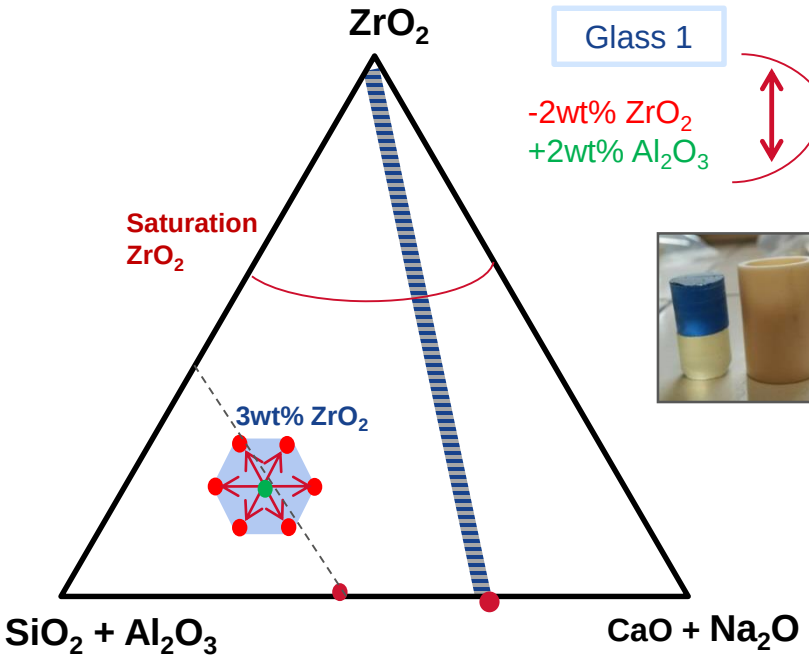
Macroscopic damage



Claireaux et al (GCA 2016)

/

DIFFUSION EXPERIMENT



Glass 1

-2wt% ZrO_2
+2wt% Al_2O_3

Glass 2

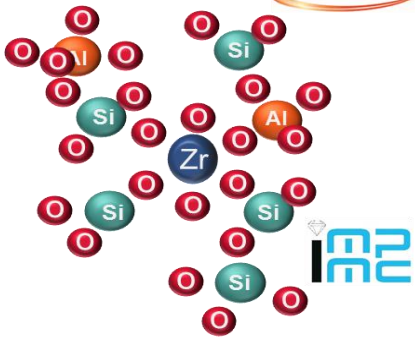
+2wt% ZrO_2
-2wt% Al_2O_3

1200°C

EPMA Profile

Structural Analysis

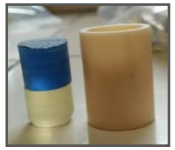
XANES
EXAFS
RMN + Raman



Central composition (wt%)

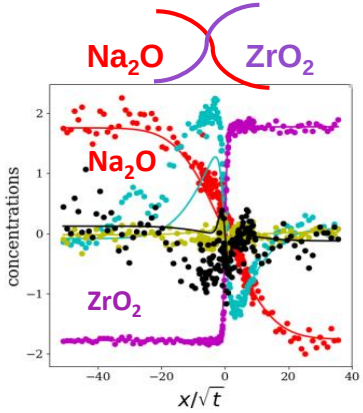
SiO_2	Na_2O	CaO	Al_2O_3	ZrO_2
62%	12%	10%	12%	3%

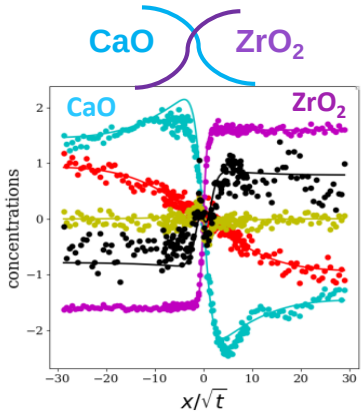
DIFFUSION EXPERIMENT

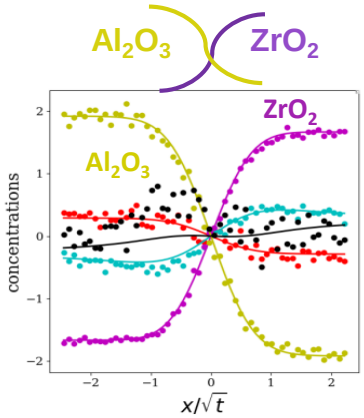


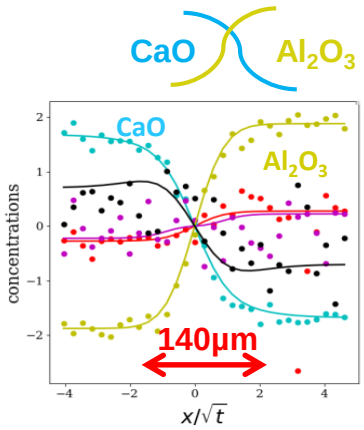
1200°C

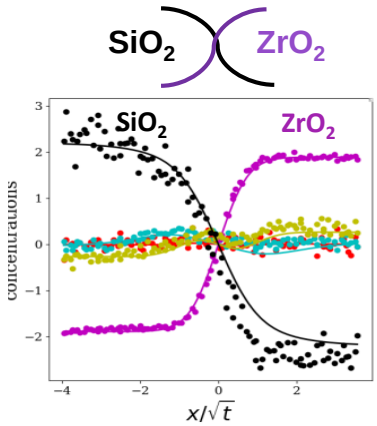
EPMA Profile

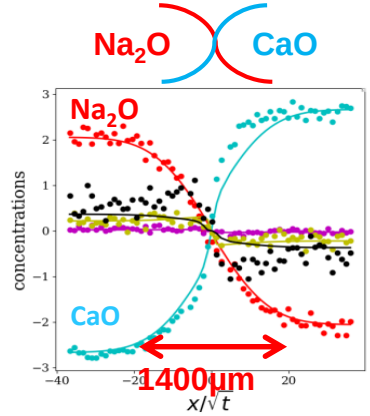


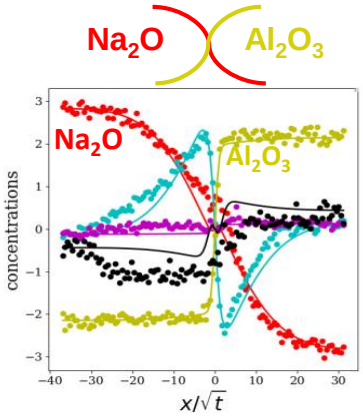












$$D = \begin{array}{c} \\ Na \\ Ca \\ Zr \\ Al \end{array} \begin{array}{c} \begin{array}{cccc} Na & Ca & Zr & Al \end{array} \\ \begin{bmatrix} 39,8 & -6,24 & -1,07 & -0.93 \\ -42,38 & 7,38 & 1,42 & 10,26 \\ 0,51 & 0,06 & 0,17 & -0,06 \\ -0,23 & -0,12 & 0,05 & 0,03 \end{bmatrix} \end{array}$$

SAINT-GOBAIN

MATRIX ANALYSIS AND EXCHANGE REACTION

Diffusion Matrix

Eigenvectors

$$\begin{pmatrix} D_{Na,Na} & D_{Na,Ca} & D_{Na,Zr} & D_{Na,Al} \\ D_{Ca,Na} & D_{Ca,Ca} & D_{Ca,Zr} & D_{Ca,Al} \\ D_{Zr,Na} & D_{Zr,Ca} & D_{Zr,Zr} & D_{Zr,Al} \\ D_{Al,Na} & D_{Al,Ca} & D_{Al,Zr} & D_{Al,Al} \end{pmatrix} = [D] = [P][\Lambda][P]^{-1}$$

Exchange reaction

Eigenvalues

3 wt% ZrO_2

$0.95\ Na_2O \leftrightarrow 1.1 CaO$ λ = 43

$0.8\ SiO_2 + 0.1\ Al_2O_3 \leftrightarrow 1.1\ CaO$ λ = 1

$0.9\ SiO_2 + 0.7\ CaO \leftrightarrow 0.65\ Al_2O_3 + 0.2\ ZrO_2 + 0.15\ Na_2O$ λ = 0,1

$0.3\ CaO + 0.5\ ZrO_2 \leftrightarrow 0.6\ Al_2O_3 + 0.2\ SiO_2 + 0.15\ Na_2O$ λ = 0,06

0 wt% ZrO_2

(Claireaux et al 2016)

$Na_2O \leftrightarrow CaO$

$0.5\ SiO_2 + 0.25\ Al_2O_3 \leftrightarrow CaO$

$0.2\ SiO_2 + CaO \leftrightarrow 1\ Al_2O_3$

Low perturbation of exchange reactions by Zr

MATRIX ANALYSIS AND EXCHANGE REACTION

Eigenvalues

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$$0.3\ CaO + 0.5\ ZrO_2 \leftrightarrow 0.6\ Al_2O_3 + 0.2\ SiO_2 + 0.15\ Na_2O$$

λ = 47.2

λ = 1.07

λ = 0,18

λ = 0,06

λ = 24.5

λ = 0.58

λ = 0.3

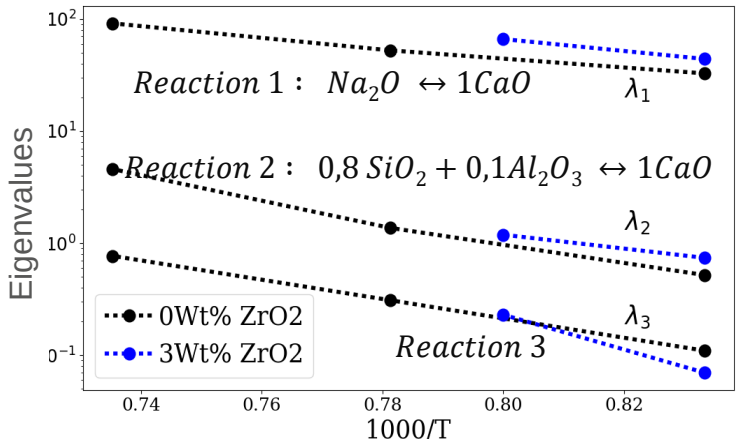
0 wt% ZrO_2

(Claireaux et al 2016)

$$Na_2O \leftrightarrow CaO$$

$$0.5\ SiO_2 + 0.25\ Al_2O_3 \leftrightarrow CaO$$

$$0.2\ SiO_2 + CaO \leftrightarrow 1\ Al_2O_3$$

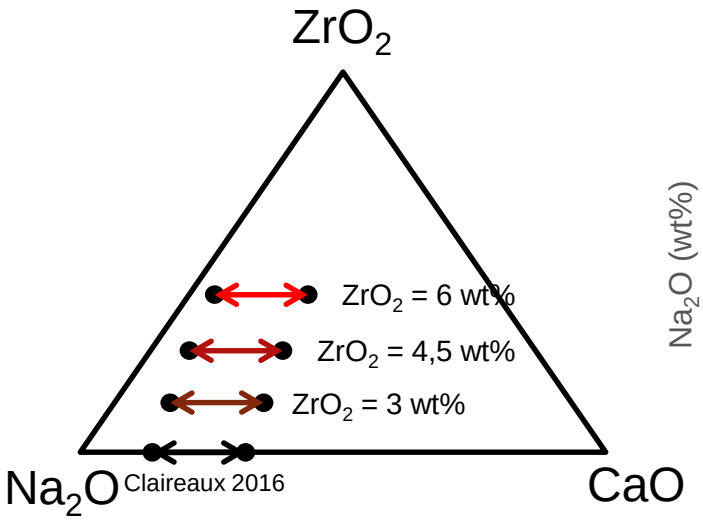


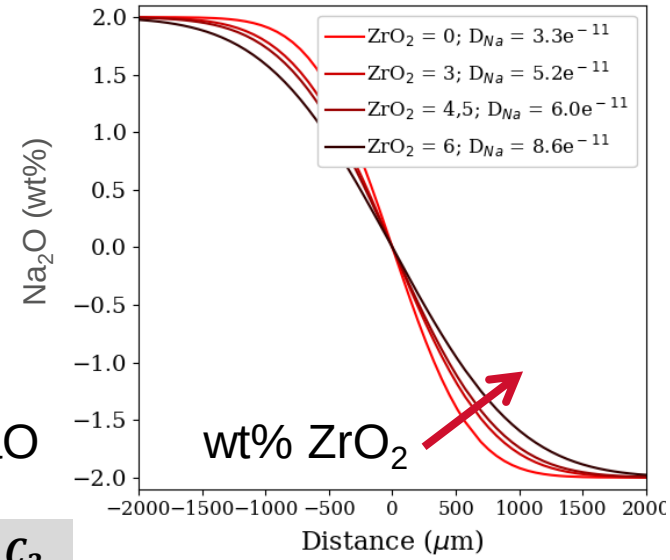
Zr increases the glass viscosity

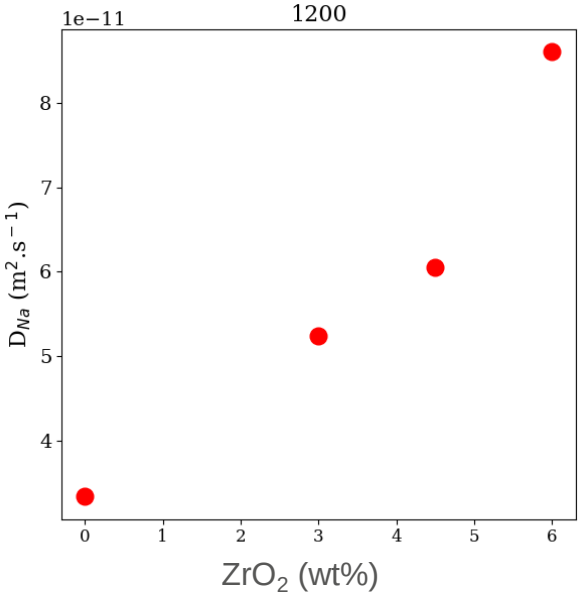
But

Increases the alkali exchange

ZIRCONIUM IMPACT ON THE SODIUM MOBILITY







$$C(x) = \frac{C_1 - C_2}{2} erf\left(\frac{x}{2\sqrt{Dt}}\right) + \frac{C_1 - C_2}{2}$$

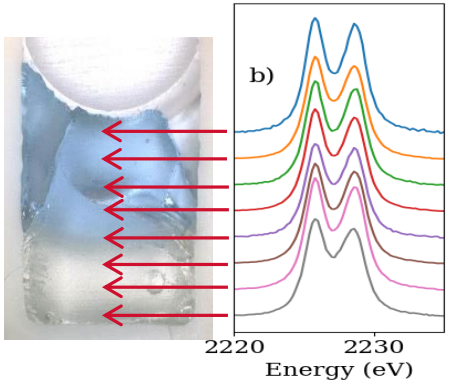
In aluminosilicate glass Zr increases Na mobility

STRUCTURE MODIFICATIONS : Zr L2 EDGE XANES & RAMAN

- More Na available = Zr site better defined
- Al and Zr use Na as charge compensator

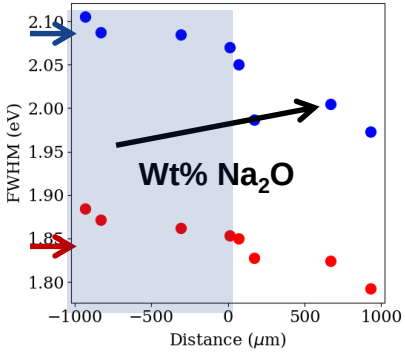
$ZrO_6^{2-} + 2\ Na^+$ ✕ $2\ AlO_2^- + 2\ Na^+$

- Competition between Al and Zr for Na as charge compensator

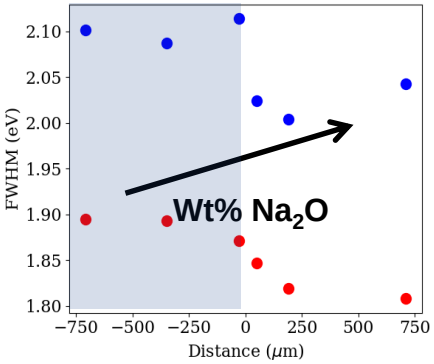


Constant 6 fold coordination

ZrO_2 ✕ Na_2O

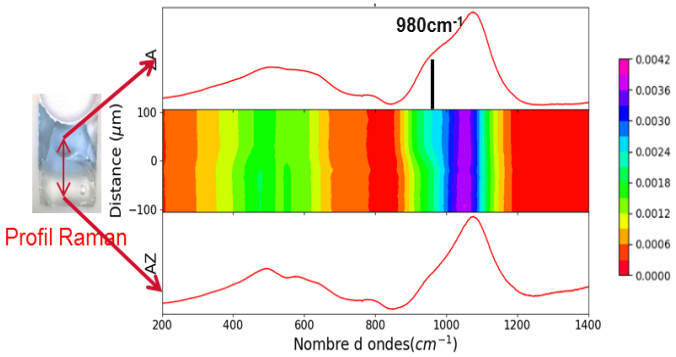


Al_2O_3 ✕ Na_2O

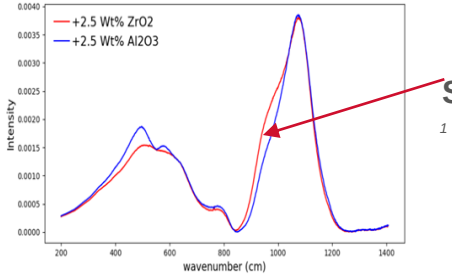


Ficheux et al., *J. Geoch. Cosm. Acta*, 2019

Al_2O_3 ✕ ZrO_2



Structural Analysis

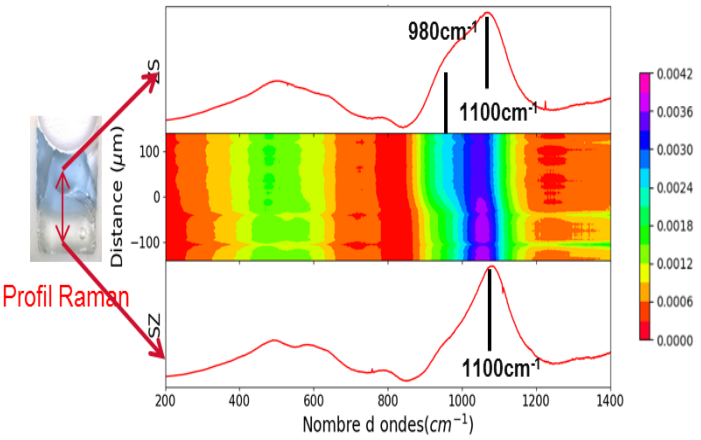


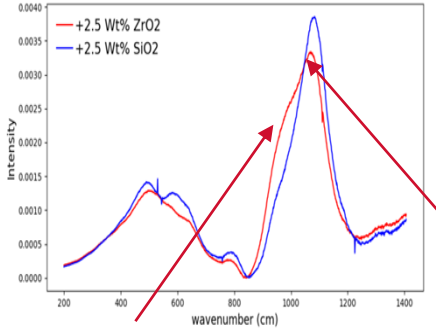
980cm^{-1} :
Si-O-Zr bending vibration[1]

[1] *Angeli et al Am Ceram Soc (2010)*

STRUCTURE MODIFICATIONS: Zr K EDGE EXAFS & RAMAN

SiO_2 ZrO_2





980cm^{-1} :
Si-O-Zr bending vibration[1]

1100cm^{-1} :
Q_3(Si) vibration decrease

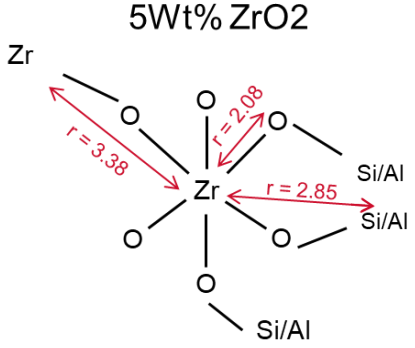
- **Some Na move from network modifier to charge compensator**

Charge compensator

ZrO_6^{2-} + 2 Na^+ ⟷ 2 Q_3(Si) + 2 Na^+

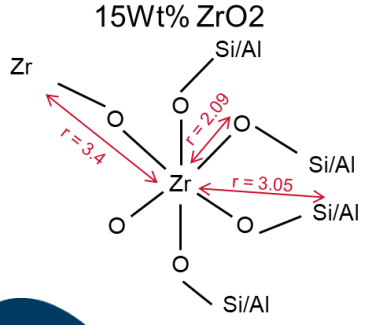
Network modifier

- **Zirconium is not randomly distributed**



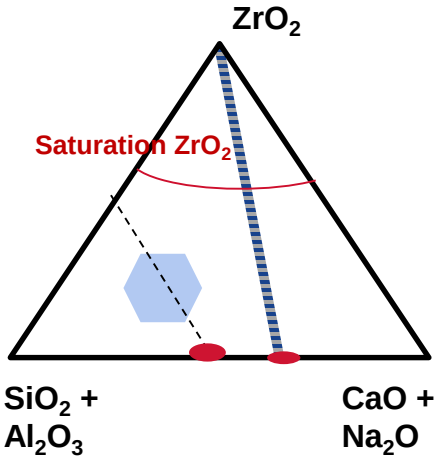
CN(Zr-Si/Al) = 4

CN(Zr-Zr) = 1.4

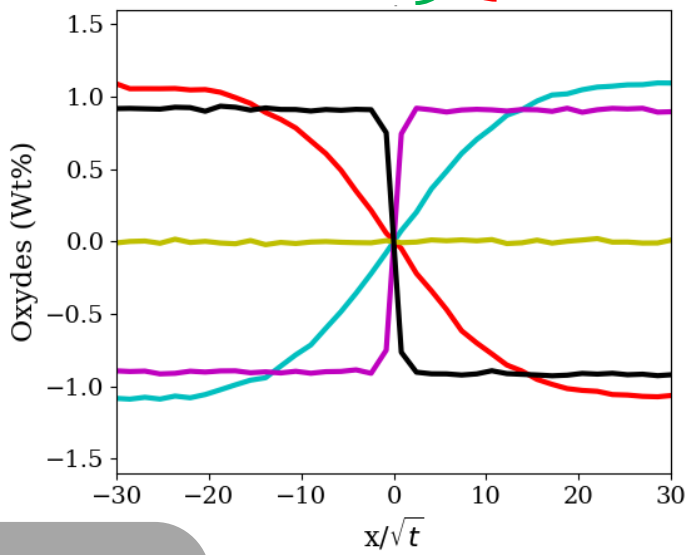


Ficheux et al., *J. Geoch. Cosm. Acta*, soumis

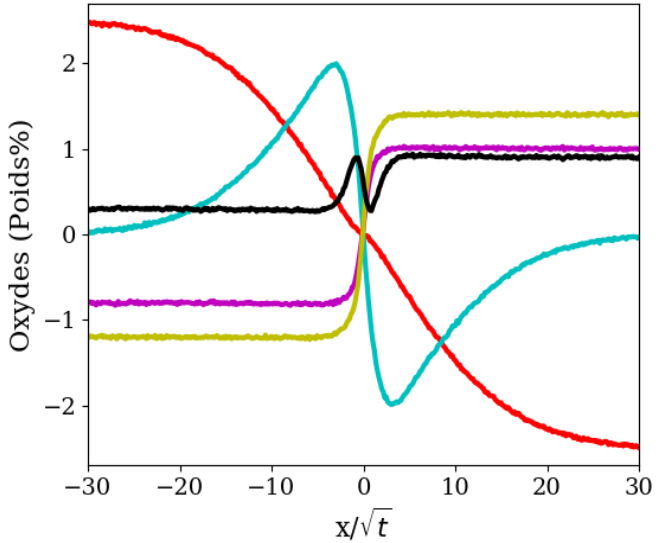
PREDICTION CAPABILITY OF THE MODEL: MULTI GRADIENT



SiO_2 , Na_2O ZrO_2, CaO



Na_2O ZrO_2, Al_2O_3



D

	Na	Ca	Zr	Al
Na	39,8	−6,24	−1,07	−0,93
Ca	−42,38	7,38	1,42	10,26
Zr	0,51	0,06	0,17	−0,06
Al	−0,23	−0,12	0,05	0,03

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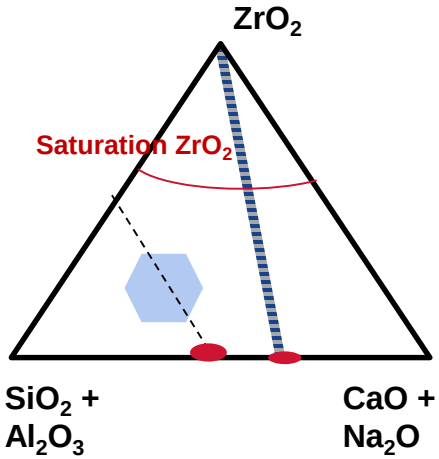
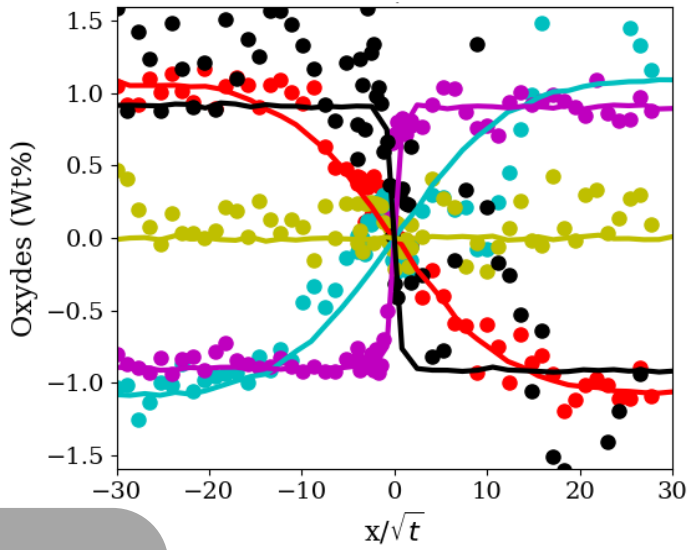
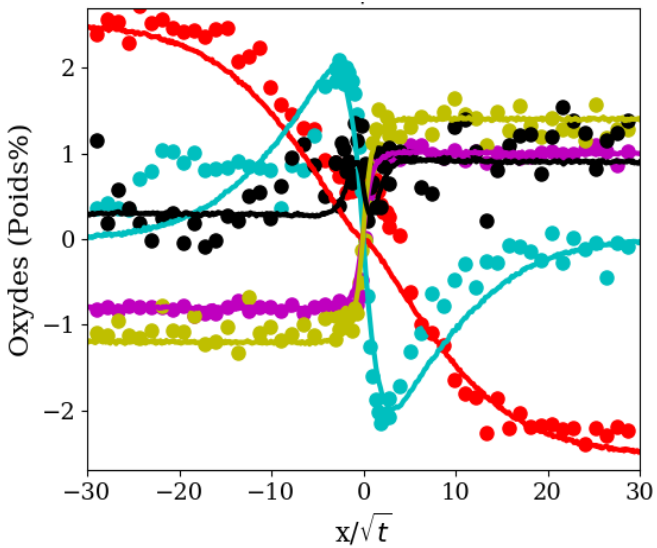


SiO_2 , Na_2O ZrO_2, CaO



Na_2O ZrO_2, Al_2O_3



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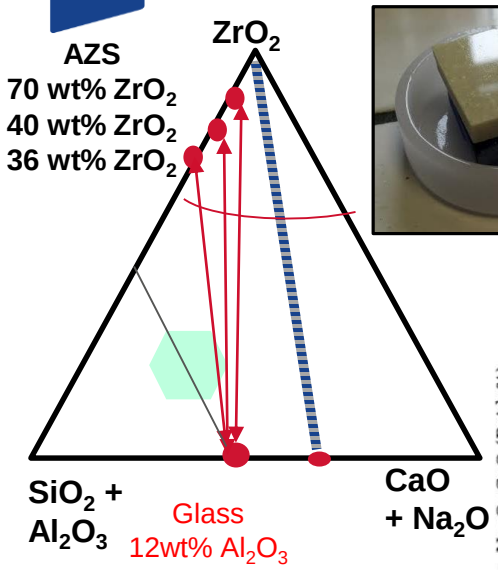
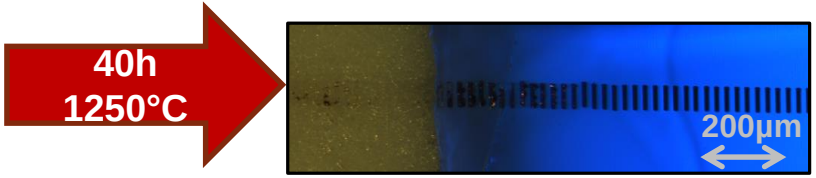
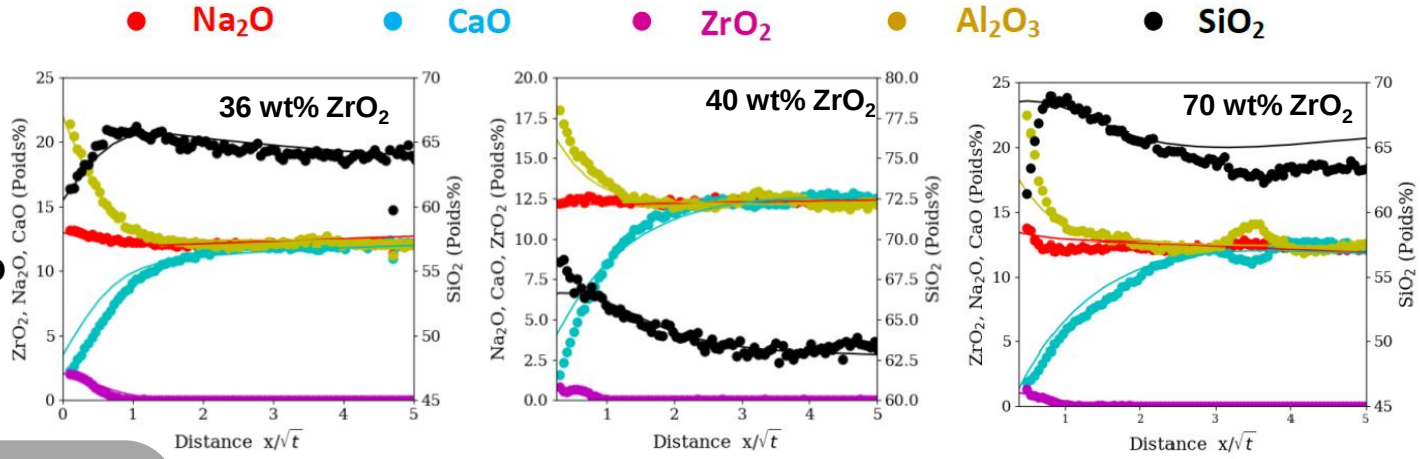
Good prediction

PREDICTION CAPABILITY OF THE MODEL







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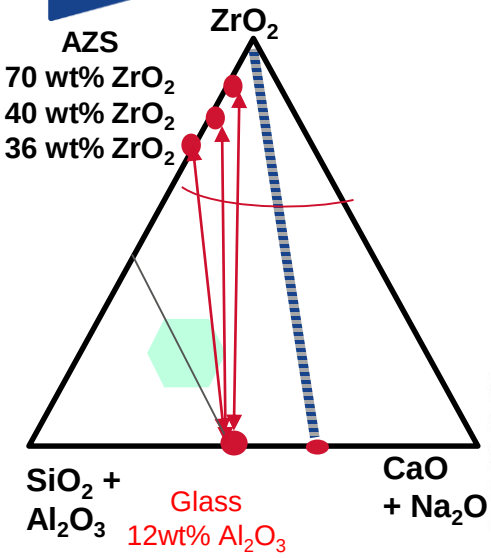
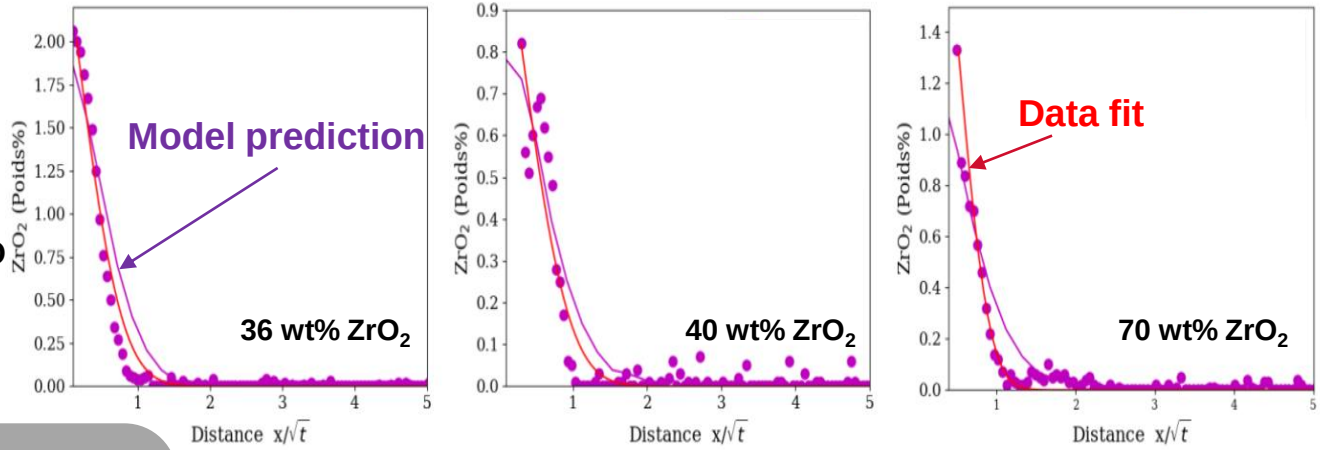
- Globally acceptable
- Decrease with ZrO_2 content

SAINT-GOBAIN

PREDICTION CAPABILITY OF THE MODEL



$$C(x) = \frac{C_1 - C_2}{2} erf\left(\frac{x}{2\sqrt{Dt}}\right) + \frac{C_1 - C_2}{2}$$



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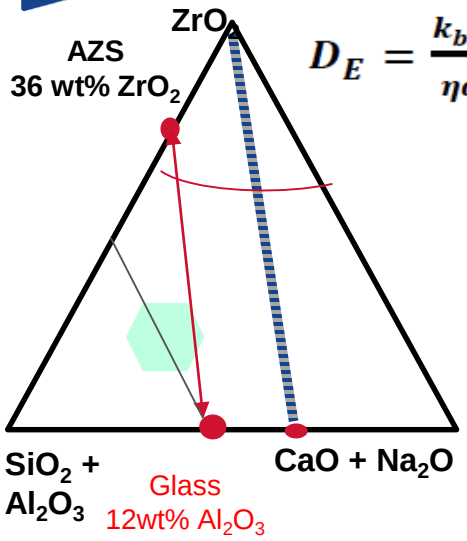
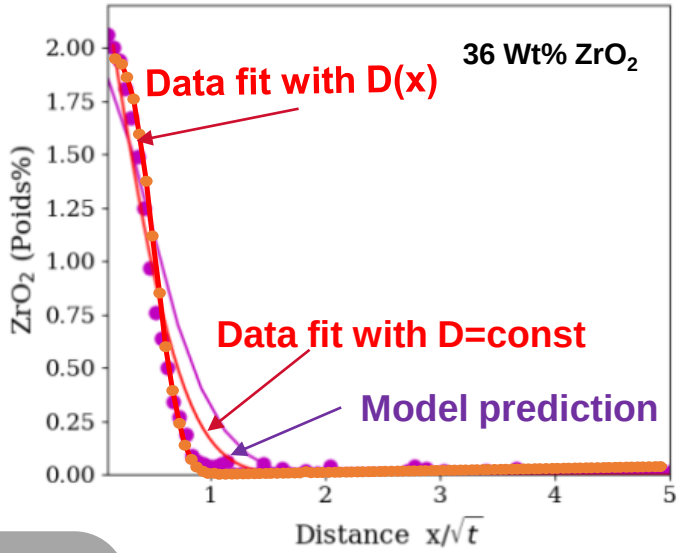
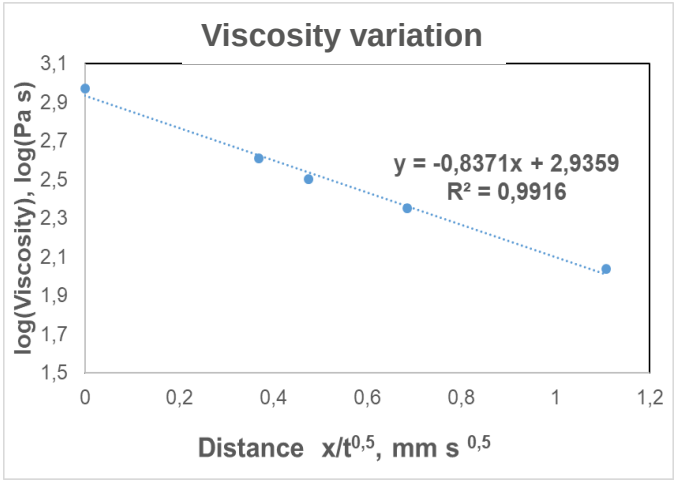
- ZrO_2 diffusion is overestimated by model
- Data fit with constant D doesn't give perfect result

PREDICTION CAPABILITY OF THE MODEL: VISCOSITY



$$D_E = \frac{k_b T}{\eta d} \rightarrow D(x) = D_{Zr,glass}\frac{\eta_{glass}}{\eta(x)} \rightarrow C(x) = 0,5C_{glass}\left(1 + erf\left(\frac{x}{2\sqrt{D(x)t}}\right)\right)$$





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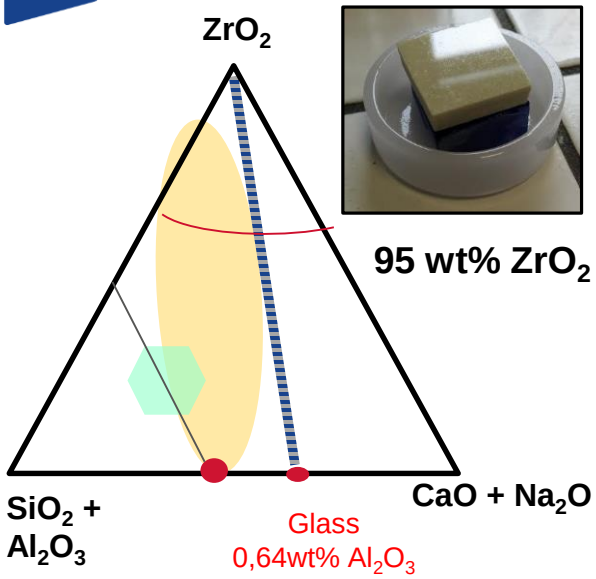
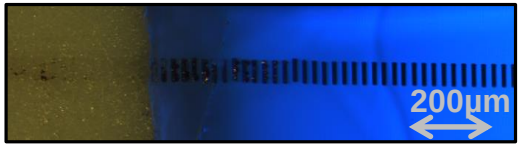
Ca	−42,38	7,38	1,42	10,26
Zr	0,51	0,06	0,17	−0,06
Al	−0,23	−0,12	0,05	0,03

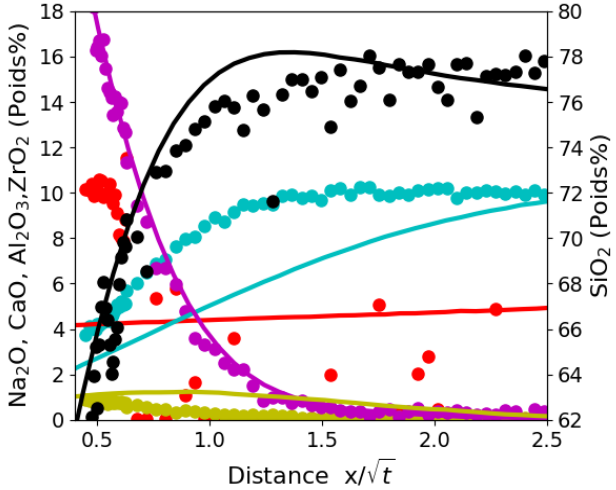
- **Data fit with D scaled by viscosity gives better result**

PREDICTION CAPABILITY OF THE MODEL



40h 1250°C



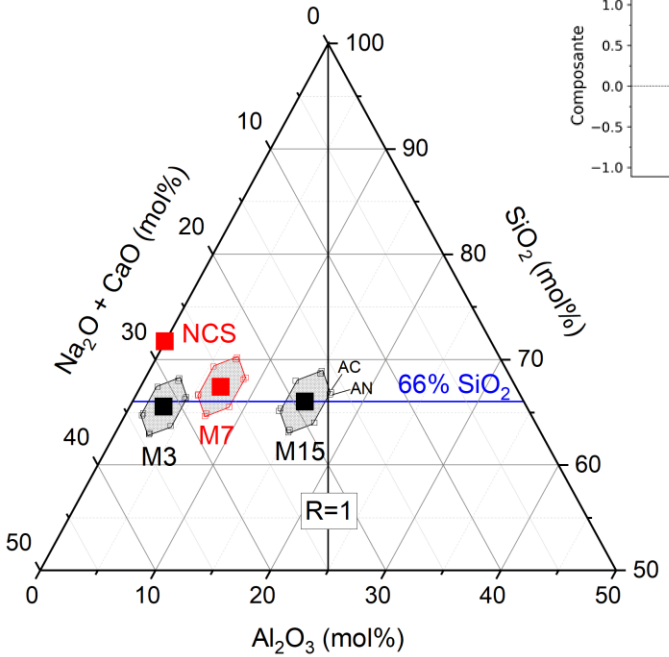


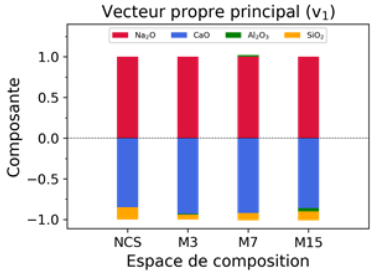
$$D = \begin{array}{c} \\ Na \\ Ca \\ Zr \\ Al \end{array} \begin{array}{c} \begin{array}{cccc} Na & Ca & Zr & Al \end{array} \\ \begin{bmatrix} 39,8 & -6,24 & -1,07 & -0,93 \\ -42,38 & 7,38 & 1,42 & 10,26 \\ 0,51 & 0,06 & 0,17 & -0,06 \\ -0,23 & -0,12 & 0,05 & 0,03 \end{bmatrix} \end{array}$$

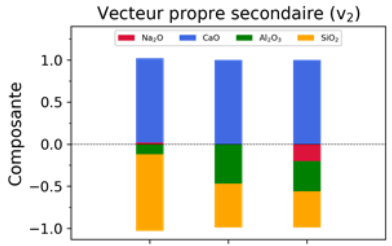
- Good prediction of ZrO_2 profile
- For others elements: behaviors not correctly predicted (high Al variation?)

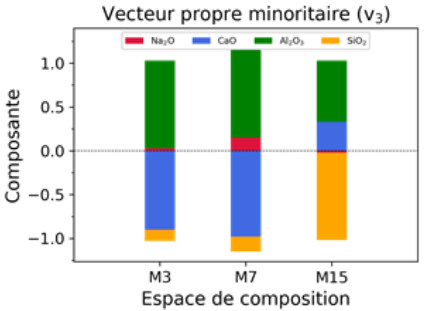
ALUMINIUM IMPACT ON THE DIFFUSION MATRIX

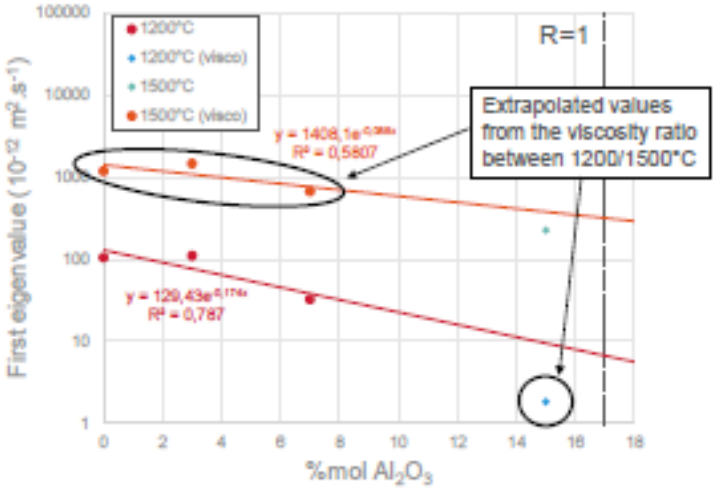
MAXIME JACQUEMIN, PHD, 2021











- From this data, we are able to retrieve an exponential dependence of the main eigenvalues to the Al_2O_3 content

CONCLUSION

- Good prediction
- Zr increases the mobility of alkali

- Globally good prediction of mobility
- Quality deceases with Zr content
- Viscosity gradient should be taken into account to increase the prediction quality

- Good prediction of ZrO2 profile
- Some complex behaviors not correctly predicted: Al impact

THANK YOU FOR YOUR ATTENTION