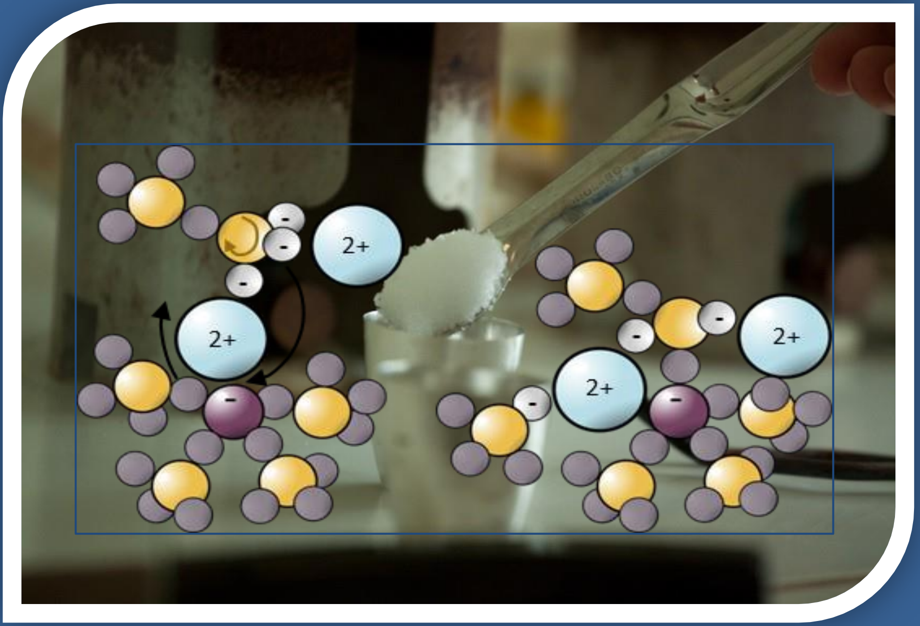


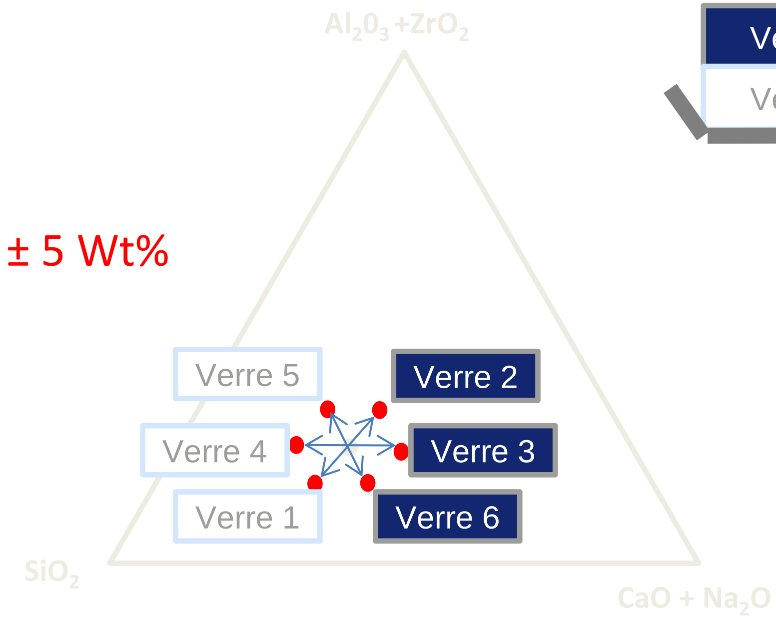
Relation diffusion activité chimique dans les verres d’oxydes

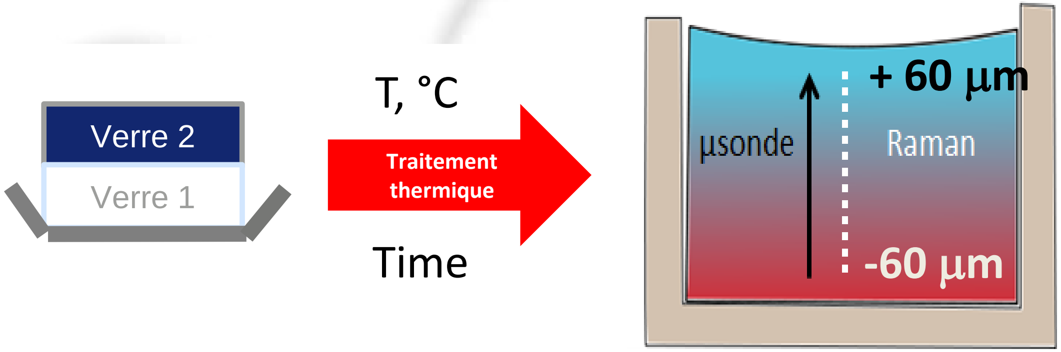
E.Burov, E.Gouillart, M.Ficheux, Q.Tissier

SVI, Unité Mixte CNRS/Saint-Gobain SVI

DIFFUSION MODEL AND DATA

- $Na_2O - CaO - SiO_2$ (NCS, W. Woelffel) **6 Glasses => 3 couples**
- $Na_2O - Al_2O_3 - SiO_2$ (NAS, V. Pukhkaya) **6 Glasses => 3 couples**
- $Na_2O - CaO - Al_2O_3 - SiO_2$ (NCAS, C. Claireaux) **12 Glasses => 6 couples**
- $Na_2O - CaO - Al_2O_3 - SiO_2 - ZrO_2$ (NCASZ, M. Ficheux) **20 Glasses => 10 couples**
- $Na_2O - B_2O_3 - SiO_2$ (NBS, H. Pablo) **6 Glasses => 3 couples**

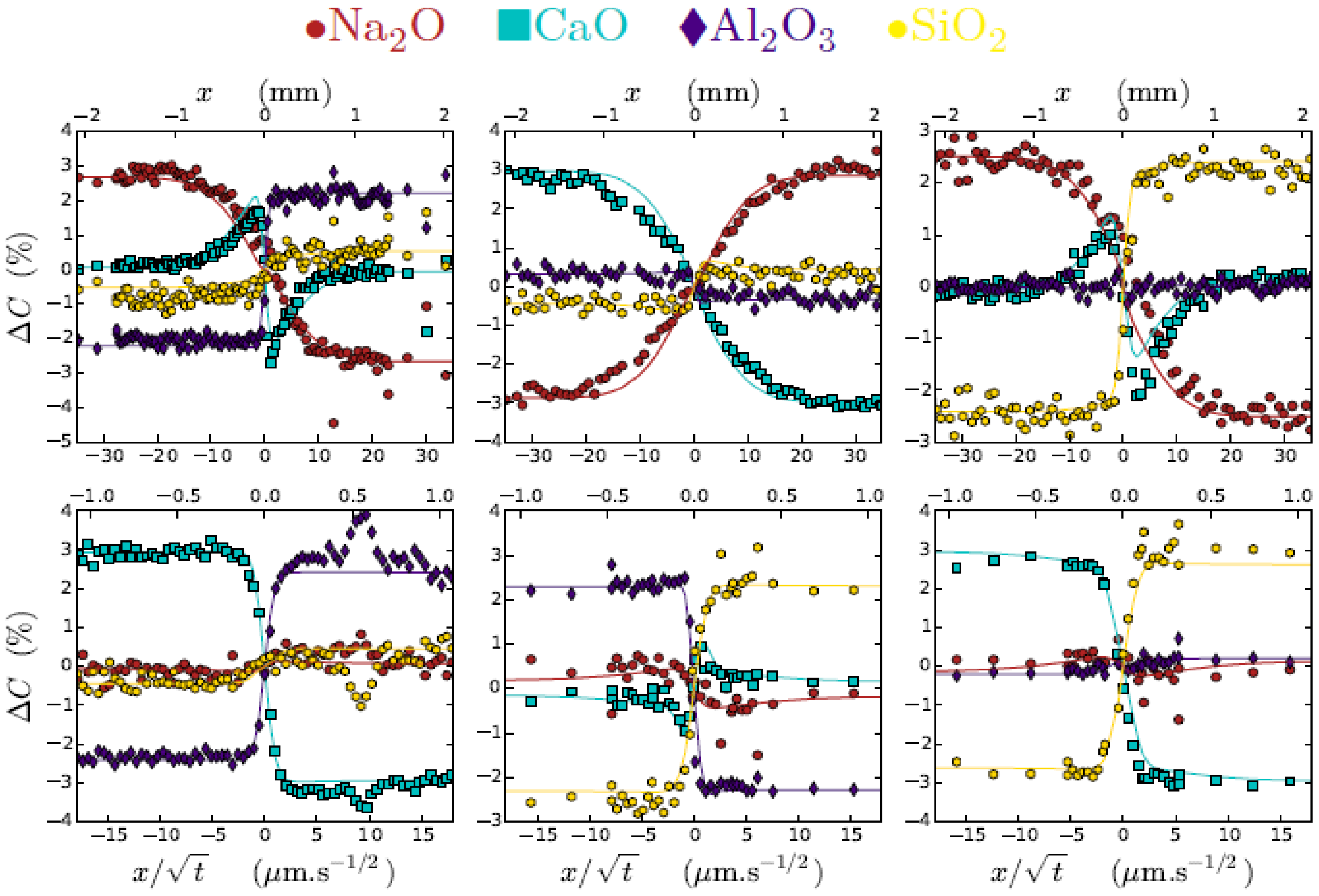




A lot of glass composition!

DIFFUSION MODEL AND DATA

Plus de dix compositions par une couple de diffusion,



[Claireaux et al., 2016] GCA

DIFFUSION MODEL AND DATA

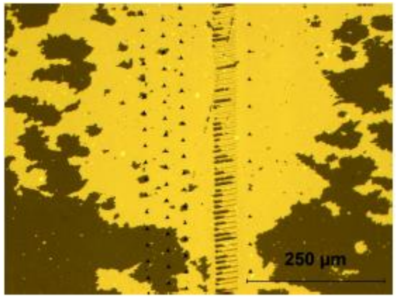
Important Data set of glass composition

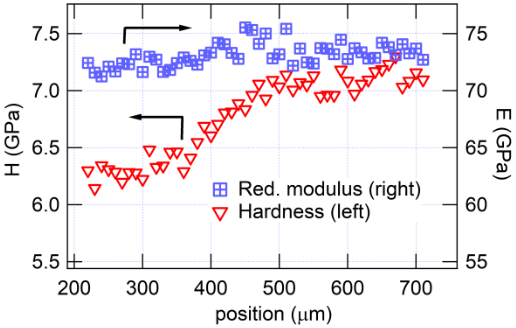
Study Properties vs composition

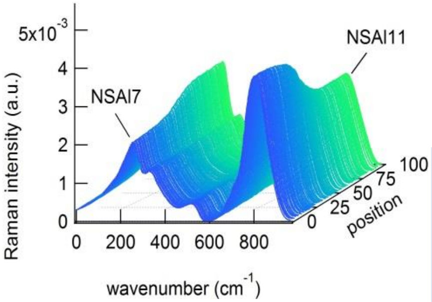
Diffusion model for multicomponent systems

NAS plasticity study

V. Pukhkaya & E.Bartel, GOMD, 2018







- ➢ **Gouillart E.**

Atelier de Diffusion, 13sep. 2018

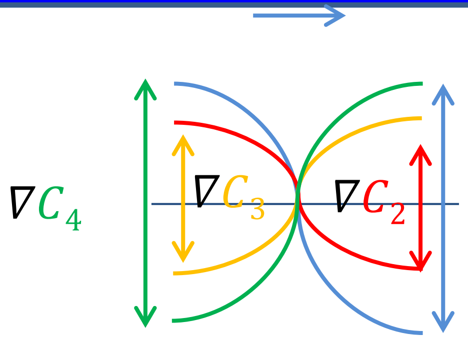
HDR, 19 octobre 2018

- ➢ **Ficheux M. Thèse en cours, soutenance fin année**
- ➢ **Projet ANR MAGI:**

2 thèses en démarrage

1. **Inclure aspect thermodynamique dans le modèle *prédictif***
2. **Utiliser les données des profils de diffusion pour nourrir et valider le model thermodynamique du verre**

MODEL de DIFFUSION



Fick's Law

$$\frac{\partial}{\partial t}\begin{pmatrix} C_{Na} \\ C_{Ca} \\ C_{Al} \\ C_{Si} \end{pmatrix} = \begin{pmatrix} D_{Na,Na} & D_{Na,Ca} & D_{Na,Al} & D_{Na,Si} \\ D_{Ca,Na} & D_{Ca,Ca} & D_{Ca,Al} & D_{Ca,Si} \\ D_{Al,Na} & D_{Al,Ca} & D_{Al,Al} & D_{Al,Si} \\ D_{Si,Na} & D_{Si,Ca} & D_{Si,Al} & D_{SiSi} \end{pmatrix} \frac{\partial^2}{\partial x^2}\begin{pmatrix} C_{Na} \\ C_{Ca} \\ C_{Al} \\ C_{Si} \end{pmatrix}$$

Eigenvectors :
Reaction direction
in the composition space

Eigenevalues :
Exchange frequency

Dominant eigenvector

$$Na^{+} \leftrightarrow 0,5Ca^{2+}$$

Second eigenvector (52x less frequent)

$$Ca^{2+} \leftrightarrow 0,5Al^{3+} + 0,5Si^{4+}$$

Third eigenvector (155x less frequent)

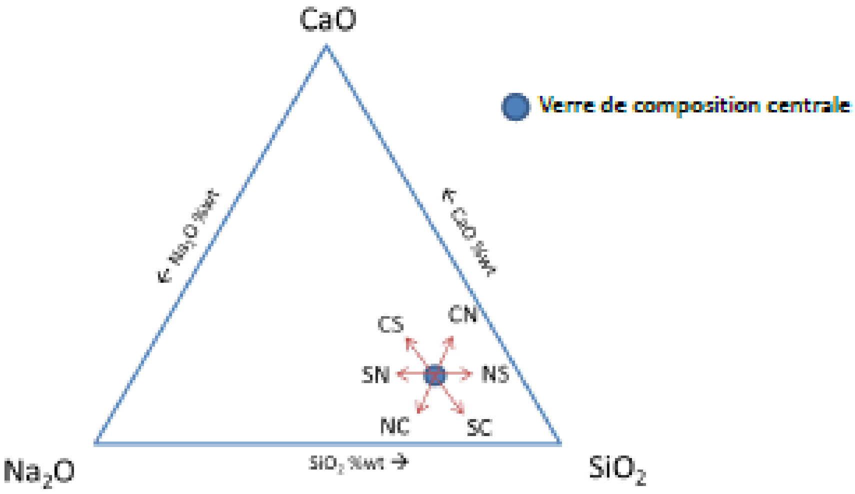
$$0,5\,Al^{3+} \leftrightarrow 0,5Ca^{2+} + 0,5Si^{4+}$$

Fourth eigenvector

$$3Ca^{2+} + 0,5Zr^{6+} \leftrightarrow 1,2Al^{3+} + 0,2Si^{4+} + 0,3Na^{+}$$

MODEL de DIFFUSION pour NCS

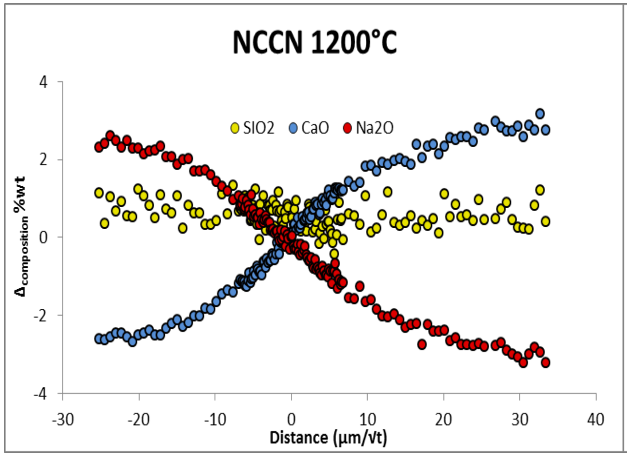
$$\frac{\partial}{\partial t}\begin{pmatrix} C_{Na} \\ C_{Ca} \\ C_{Si} \end{pmatrix} = \begin{pmatrix} D_{Na,Na} & D_{Na,Ca} & D_{Na,Si} \\ D_{Ca,Na} & D_{Ca,Ca} & D_{Ca,Si} \\ D_{Si,Na} & D_{Si,Ca} & D_{Si,Si} \end{pmatrix} \frac{\partial^2}{\partial x^2}\begin{pmatrix} C_{Na} \\ C_{Ca} \\ C_{Si} \end{pmatrix}$$

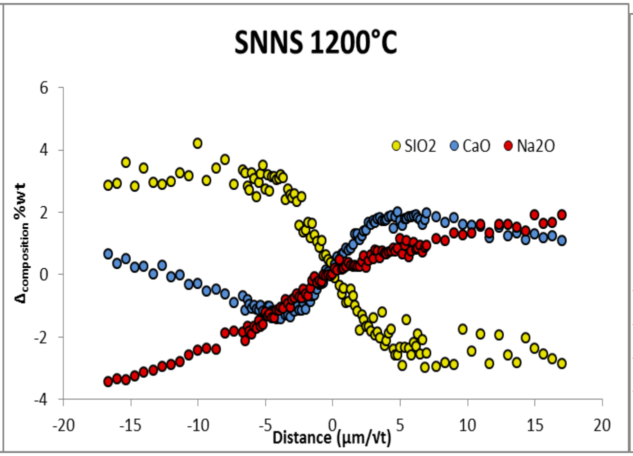


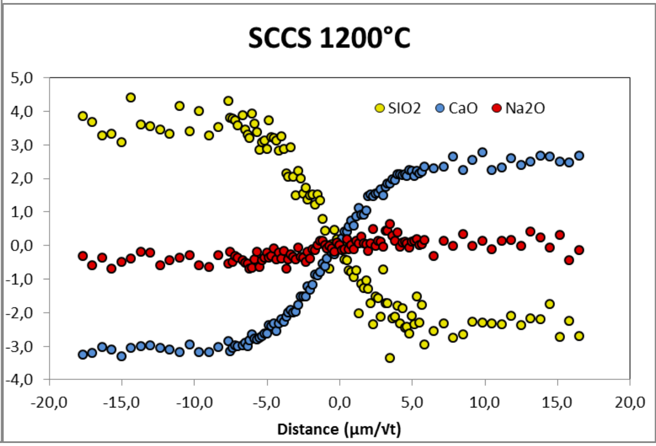
T, °C: 750, 1000, 1200, 1250, 1280

	Eléments de bases en pourcentage massique (%wt)		
	SiO_2	CaO	Na_2O
Verre central	70	13	17
SN	73 (+3)	13	14 (-3)
NS	67 (-3)	13	20 (+3)
SC	73 (+3)	10 (-3)	17
CS	67 (-3)	16 (+3)	17
NC	70	10 (-3)	20 (+3)
CN	70	16 (+3)	14 (-3)

MODEL de DIFFUSION pour NCS

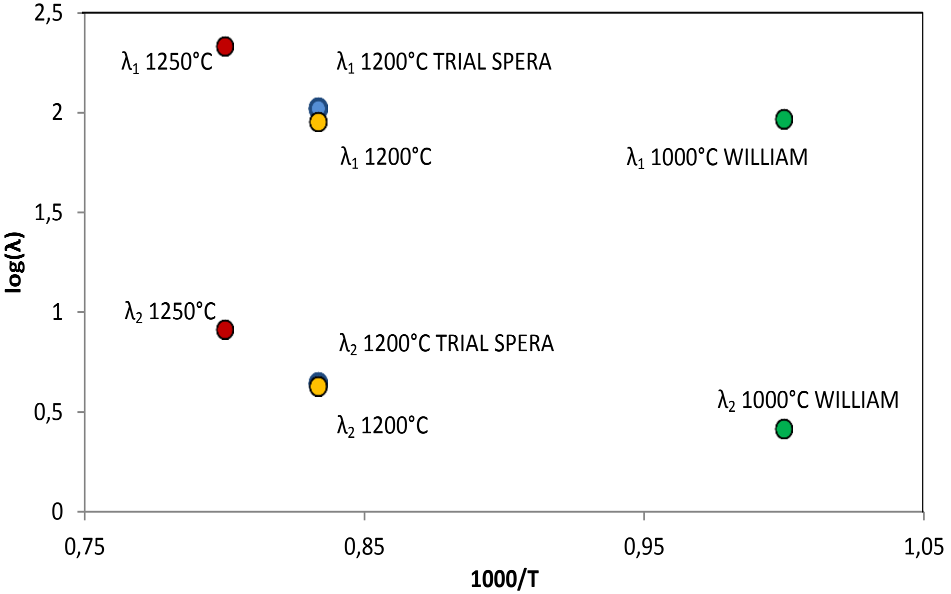






$$Na_2O \leftrightarrow 1,03CaO + 0,07SiO_2$$

$$SiO_2 \leftrightarrow 0,95CaO + 0,11Na_2O$$



Model Thermodynamique et Vecteurs propres

$$Na_2O \leftrightarrow 1,03CaO + 0,07SiO_2O$$ λ1

$$R_f = k_f a_{Na2O}$$

$$R_r = k_r a^{1.03}{}_{CaO} a^{0.07}{}_{SiO2}$$

$$R_{ech1} = \frac{k_f}{k_r} \frac{a_{Na2O}}{a^{1.03}{}_{CaO} \; a^{0.07}{}_{SiO2}} = \frac{Cinétique}{Thermod}$$

Cinétique

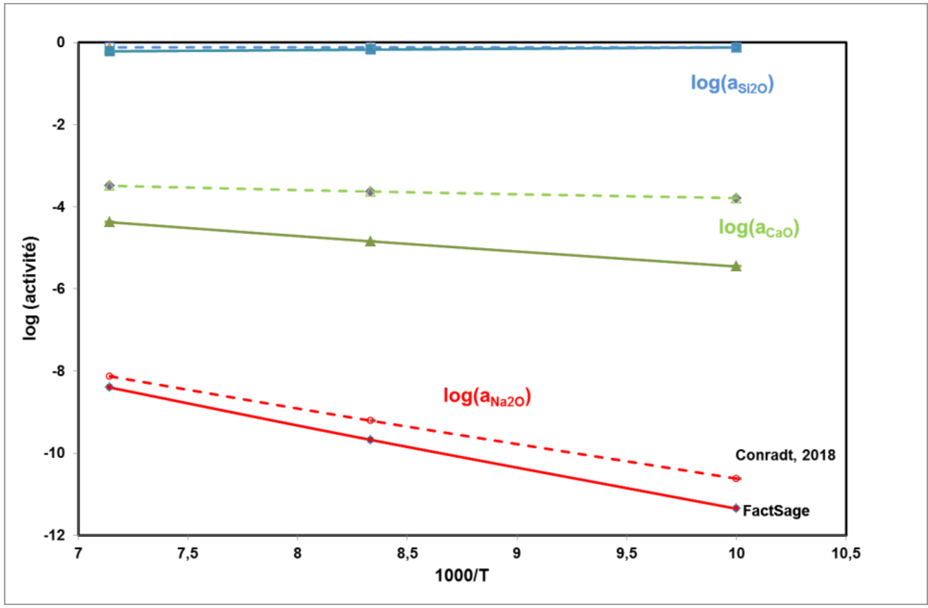
1/Keq ->Thermodynamique

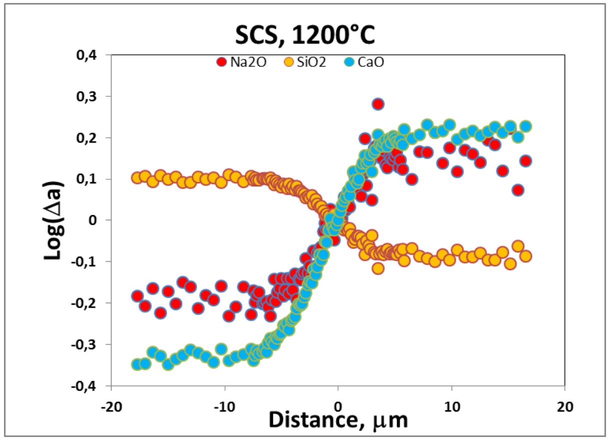
$$SiO_2 \leftrightarrow 0,95CaO + 0,11Na_2O$$ λ2

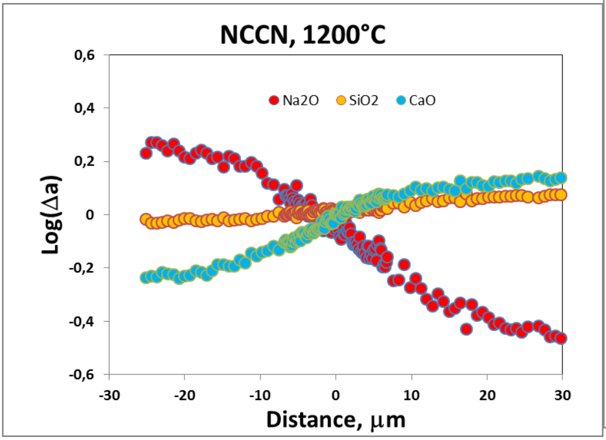
$$R_{ech2} = \frac{k_f}{k_r} \frac{a_{SiO2}}{a^{0.95}{}_{CaO} \; a^{0.11}{}_{NaO2}}$$

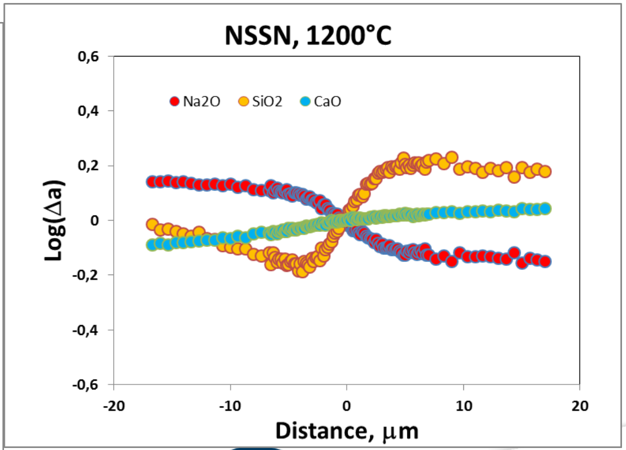
MODEL THERMODYNAMIQUE

Model Quasi-chimique des solutions



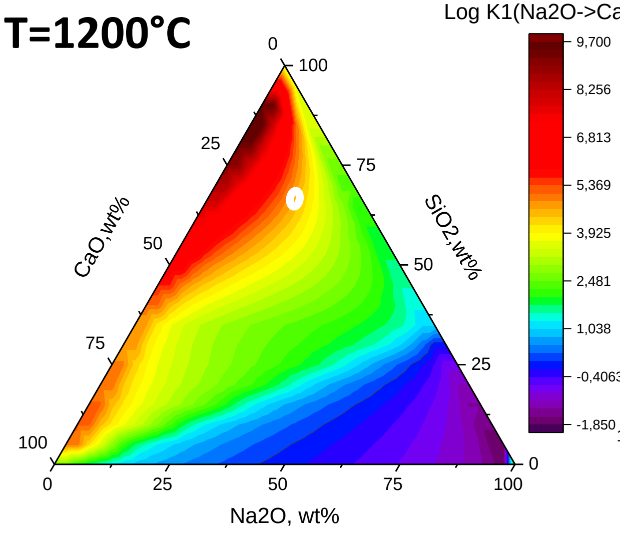


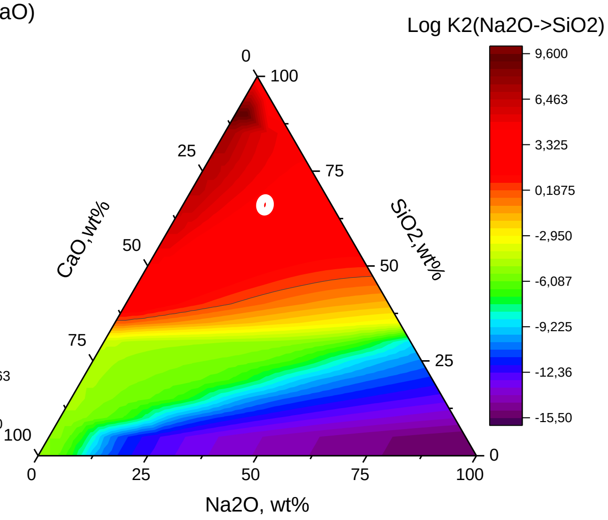


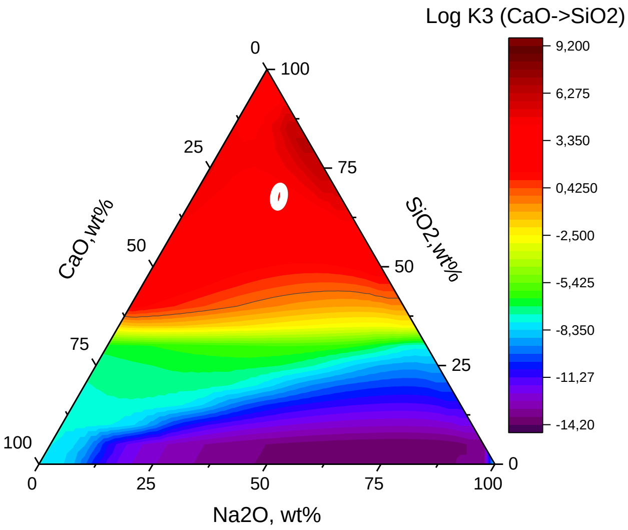


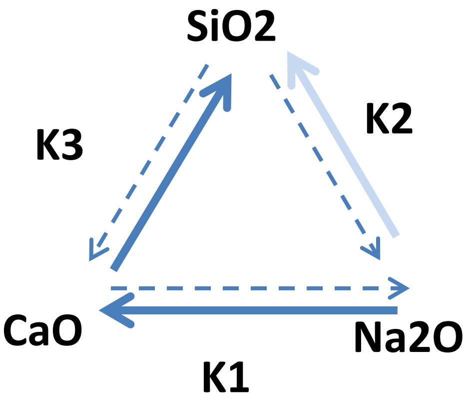
MODEL de DIFFUSION pour NCS : ECHANGE BINAIRE

T=1200°C









SiO2

K3

K2

CaO

Na2O

K1

SiO2 70% Na2O 17% CaO 13%

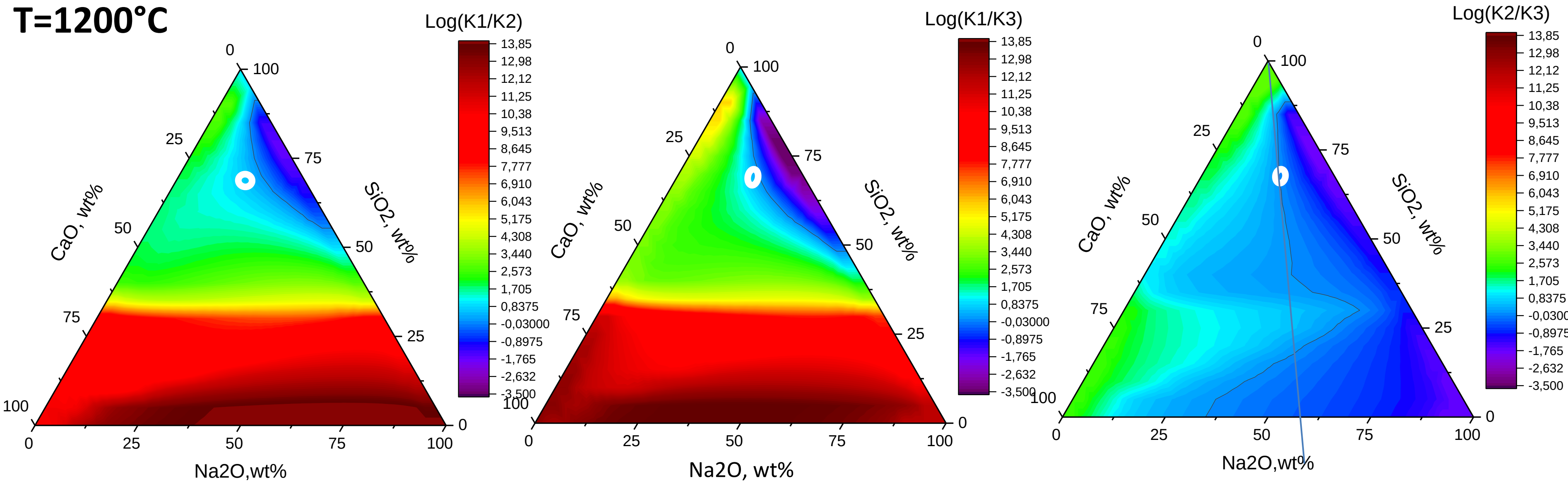
Log(K1)=4.86

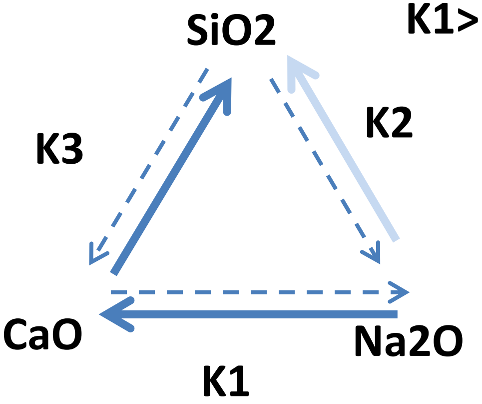
Log(K2)=8.90

Log(K3)=4.12

MODEL de DIFFUSION pour NCS: ECHANGE BINAIRE

T=1200°C





K1>K2>K3

SiO2 70% Na2O 17% CaO 13%

Log(K1/K2)=-4,86

Echange Na2O->Ca est $10^{4.86}$ plus probable que Na2O->SiO2

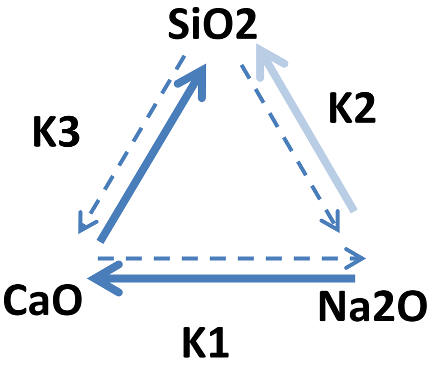
Log(K1/K3)=0.73

Echange CaO->0.5 SiO2 est $10^{0,73}$ plus probable que Na2O->CaO

Log(K2/K3)=4.7

Echange CaO->SiO2 est $10^{4.7}$ plus probable que Na2O->SiO2

MODEL DE DIFFUSION NCS A PARTIR DES ECHANGES BINAIRES



SiO2 70% Na2O 17% CaO 13%

$R1/R2=10^{4.12}$

$R1/R3=5.37$

$R3/R2=10^{4.7}$

Vecteur propre 1 :

Na2O->CaO $K1=a_{CaO}/a_{Na2O}$

Na2O->SiO2 $K2=a_{SiO2}/a_{Na2O}$

$R1/R2=10^{4.86}$

Na2O ->CaO

$$De\ matrice\ de\ diffusion:\ Na_2O \leftrightarrow 1,03CaO + 0,07SiO_2\ (Notre)$$
$$Na_2O \leftrightarrow 0,85CaO + 0,15SiO_2\ (Trial\ and\ Spera, 1994)$$

Vecteur 2:

Na2O->SiO2 $K2=a_{SiO2}/a_{Na2O}$

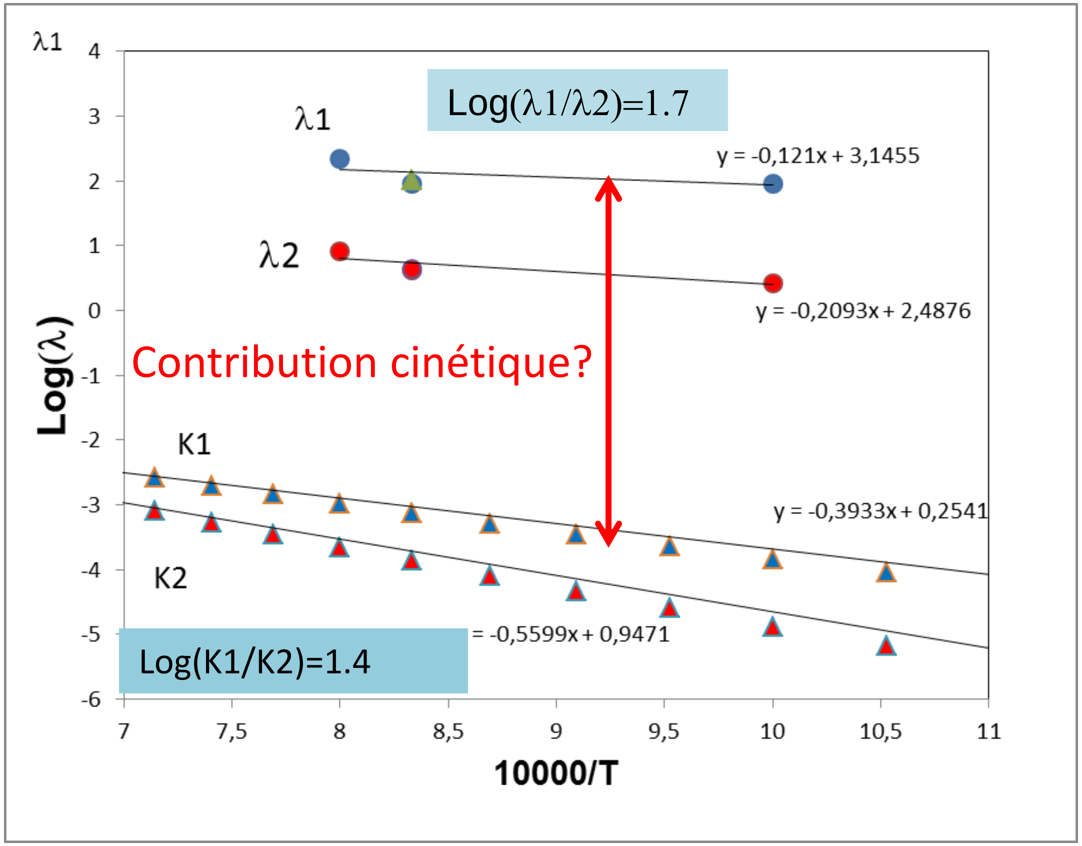
CaO->SiO2 $K3=a_{SiO2}/a_{CaO}$

$R3/R2=10^{4.7}$

CaO-> SiO2

$$Diffusion\ experiment:\ SiO_2 \leftrightarrow 0,95CaO + 0,11Na_2O$$
$$SiO_2 \leftrightarrow 0,73CaO + 0,27Na_2O\ (Trial\ and\ Spera, 1994)$$

MODEL de DIFFUSION pour NCS



Log(λ1/λ2)=1.7

Contribution cinétique?

Log(K1/K2)=1.4

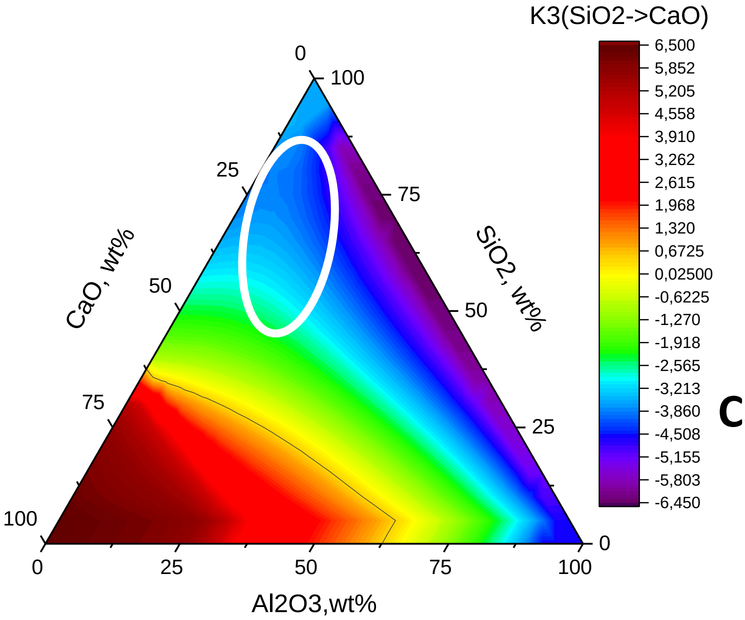
$$Na_2O \leftrightarrow 1,03\mathrm{CaO} + 0,07SiO_2O$$

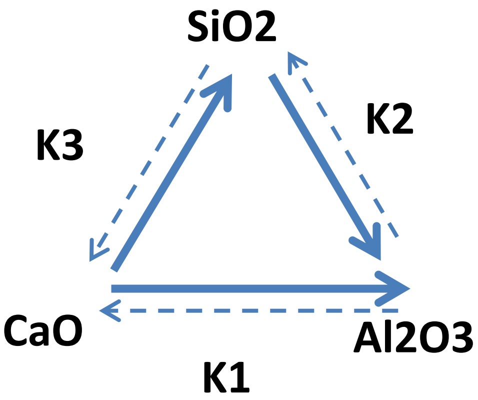
$$K_1 = \frac{a^{1.03}{}_{CaO}\ \ a^{0.07}{}_{SiO2}}{a_{Na2O}}$$

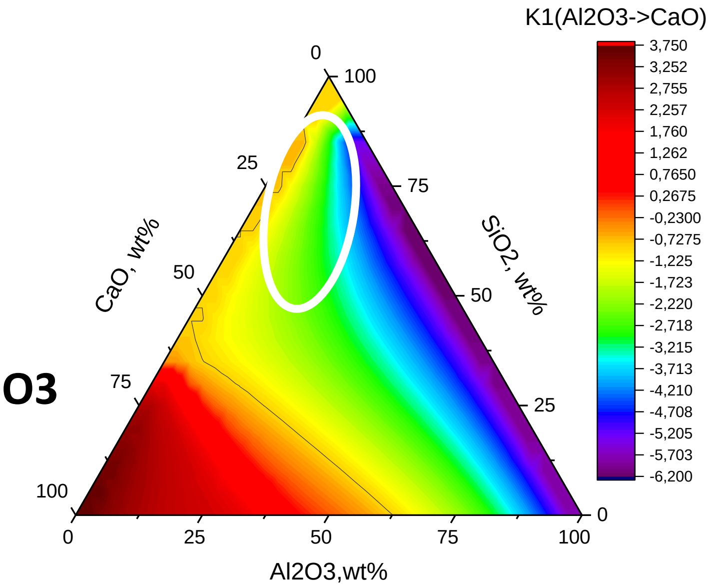
$$SiO_2 \leftrightarrow 0,95\mathrm{CaO} + 0,11Na_2O$$

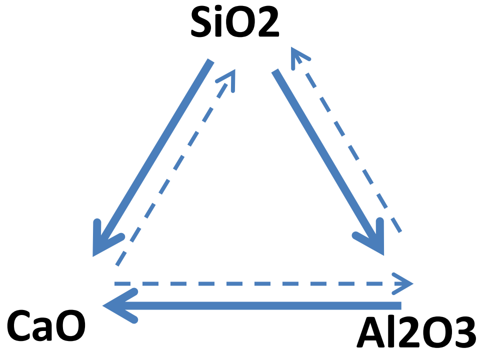
$$K_2 = \frac{a^{0.95}{}_{CaO}\ \ a^{0.11}{}_{Na2O}}{a_{SiO2}}$$

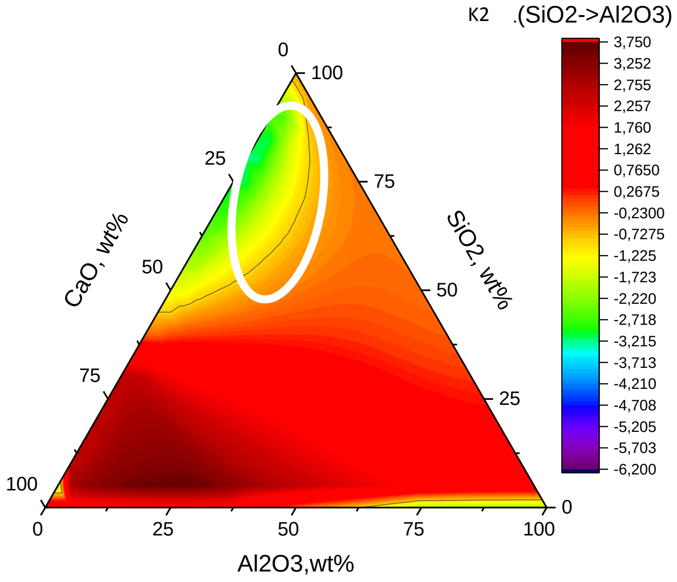
MODEL de DIFFUSION pour CAS









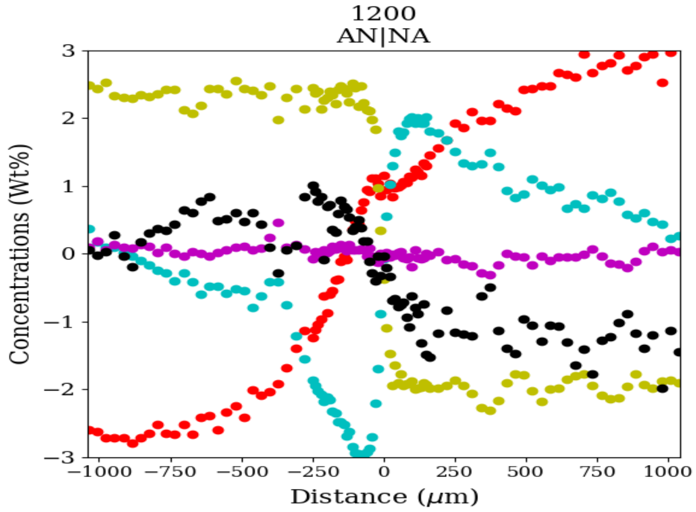


Réaction obtenu à partir de th

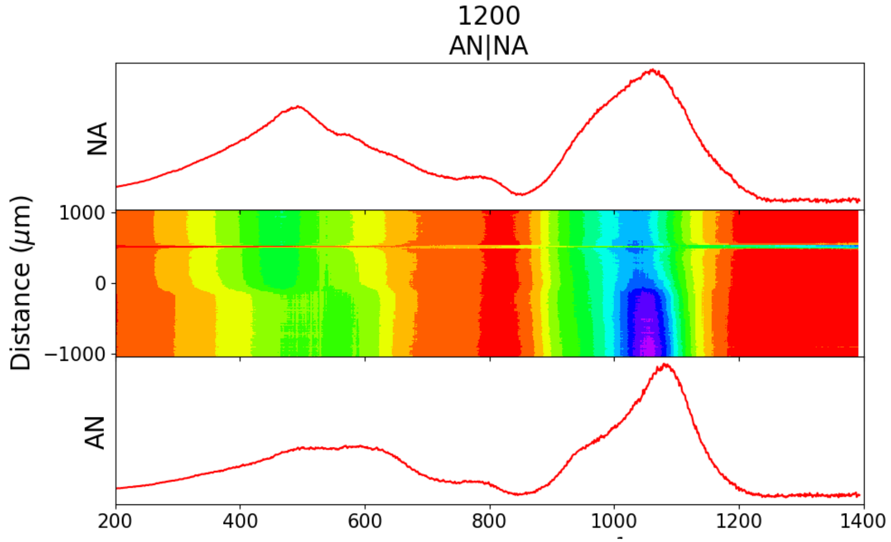
$CaO \rightarrow 0{,}5Al_2O_3 + 0{,}5SiO_2$

$SiO_2 + 0{,}15CaO \rightarrow Al_2O_3$

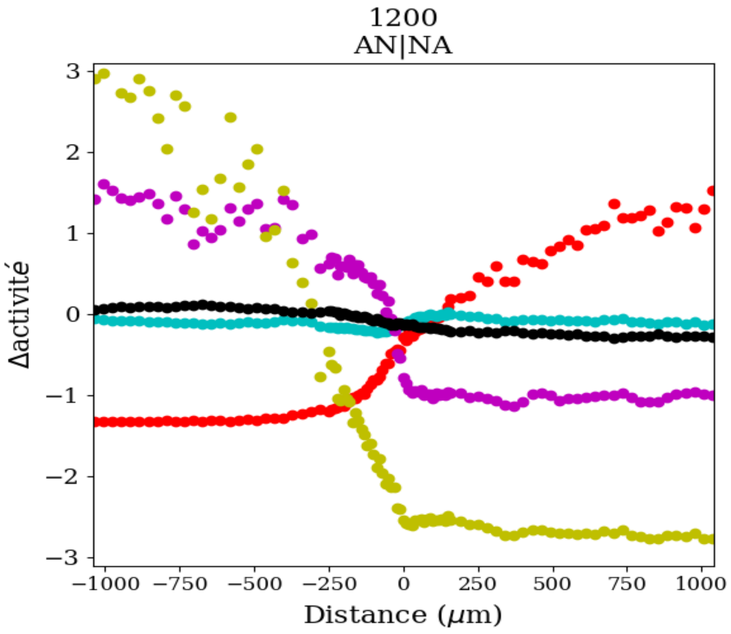
MODEL de DIFFUSION pour NCAZ



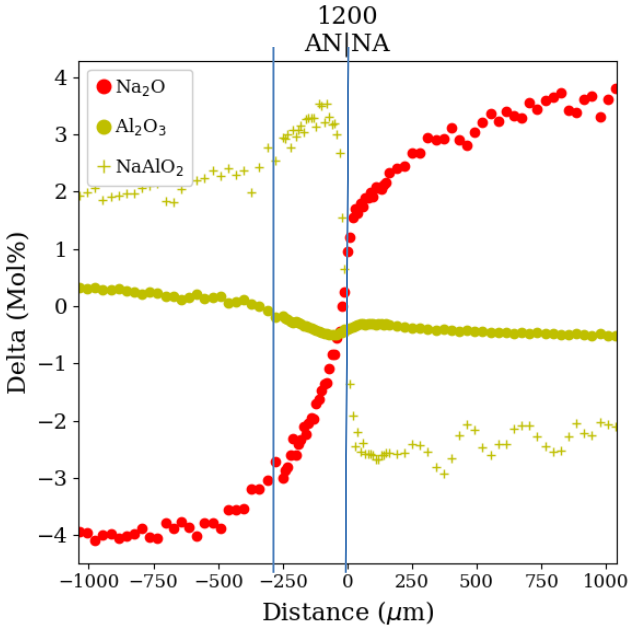
1200
AN|NA



1200
AN|NA



1200
AN|NA



1200
AN|NA

SAINT-GOBAIN

Quelques conclusions et la suite

- Expériences de diffusion donnent une large gamme des compositions => Comment les utiliser pour les modèles thermodynamiques?
- Analyse thermodynamique d’une system donne une bonne première estimation des chemins de diffusion et l’efficacité de ces échanges
- Les valeurs propres de la matrice de diffusion contient une partie non-négligeable
- Continuer avancer vers le model de la diffusion dans une system multi composante contenant compte de gradient des forces chimiques (potentiels chimiques)