

# Surfaces du verre

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# Plan

## Spécificité des couches externes du verre

sites contraints

silanols de surface

## Physisorption et chimisorption

généralités

modélisation

famille de sites

## Profil redox du verre flotté

le profil de l'étain

mesures par microscopie XAS

profils du soufre, du fer et de l'étain

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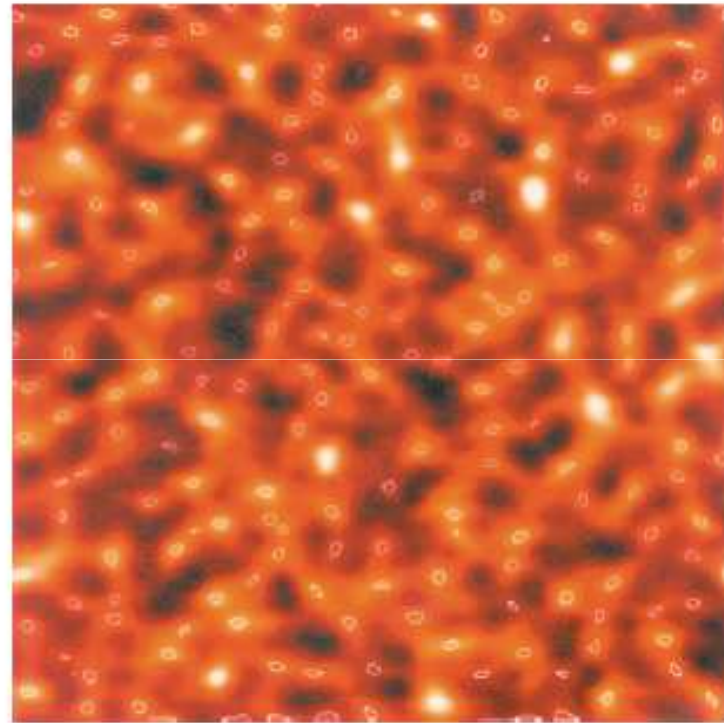
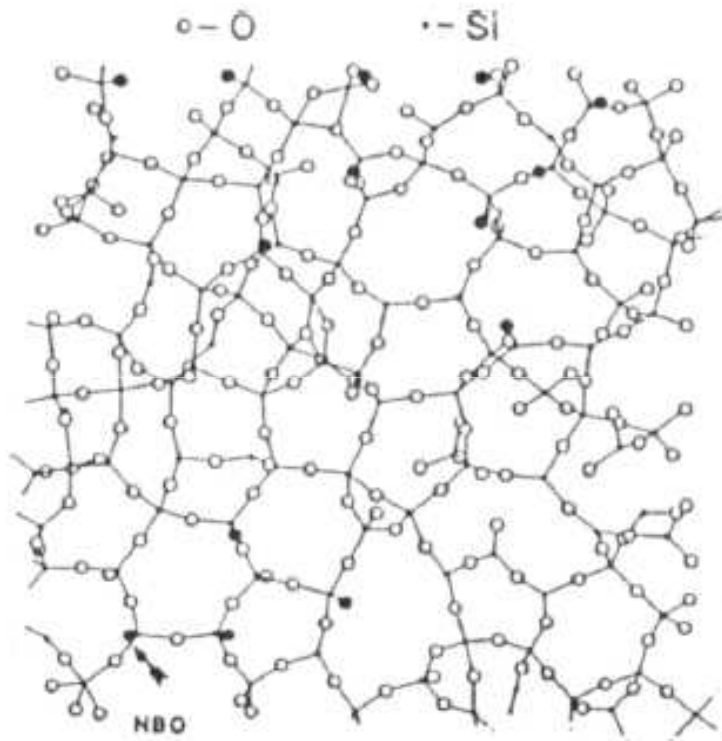
famille de sites

## Profil redox du verre flotté

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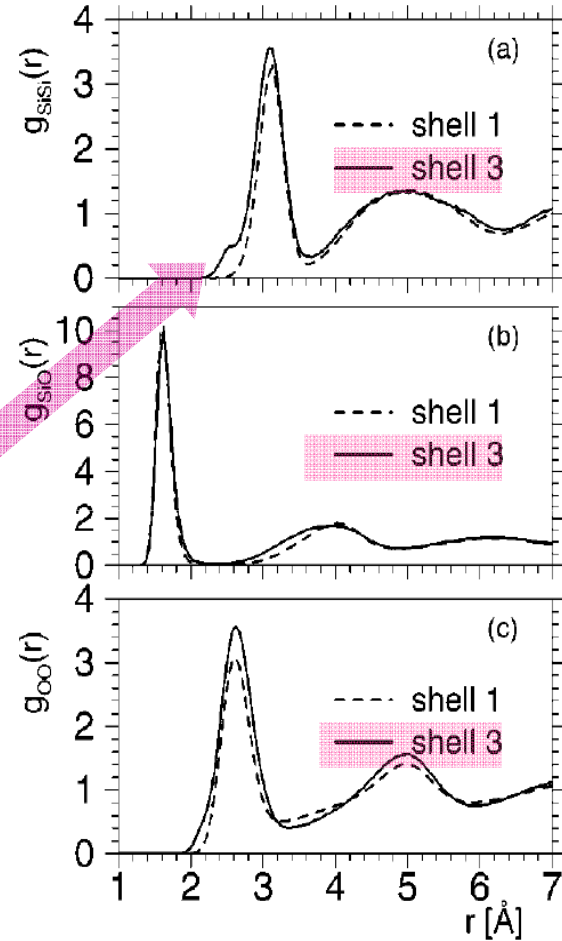
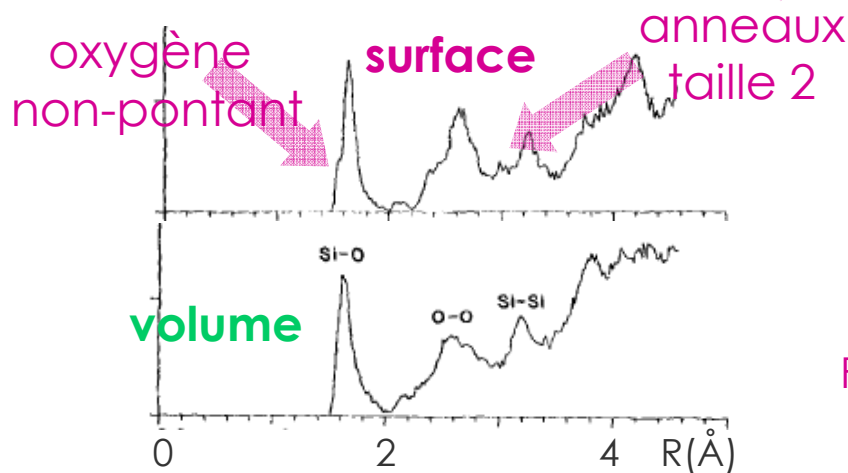
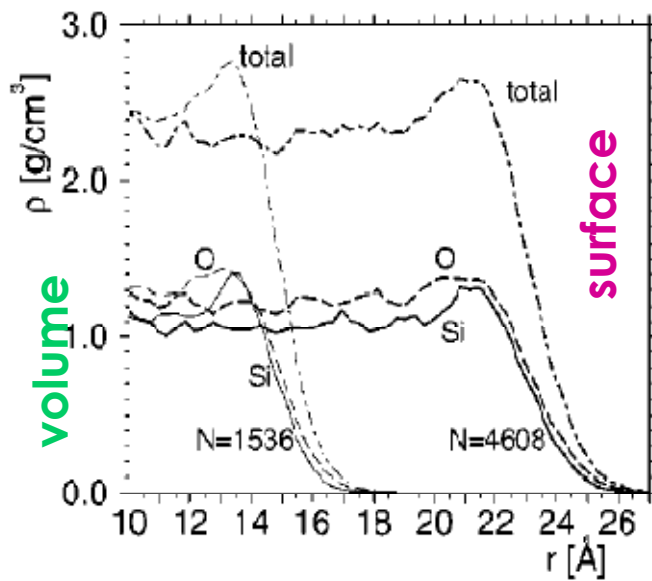
mesures par microscopie XAS

profils du soufre, du fer et de l'étain



Raberg et Wandelt, Appl. Phys. A66 (1998)

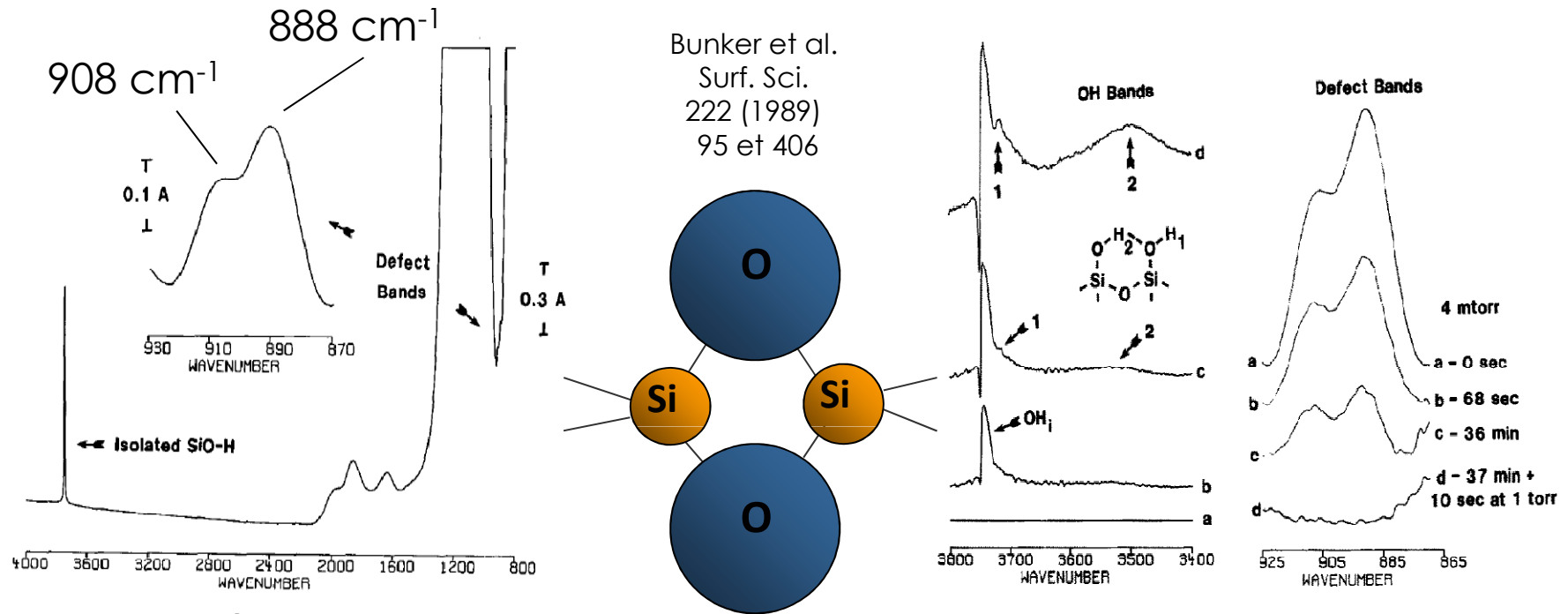
# Spécificité des couches externes des verres



Fonction de **distribution radiale S/V**  
 distance **Si-O** invariable  
 distribution plus **hétérogène**  
**nouvelle** configuration Si-Si

Roder et al., J. Chem. Phys. 114 (2001)  
 Garofalini, J. Chem. Phys. 78 (1983)

# Sites contraints – Anneaux de taille 2



espèce **superficielle**

**adsorption-désorption**

même écart de fréquence que dans le spectres IR des **cyclodisiloxanes**

déplacement en fréquence par **échange isotopique**

densité : expérience : 0.1 – 0.4 nm<sup>-2</sup>, théorie : 0.13 – 3 nm<sup>-2</sup>

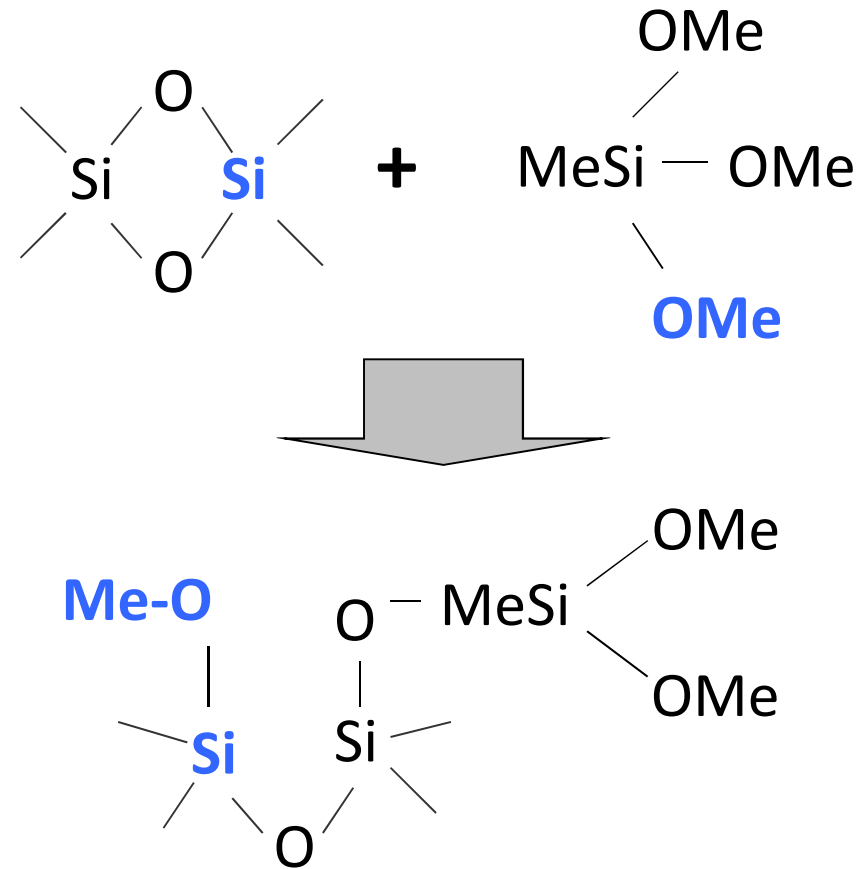
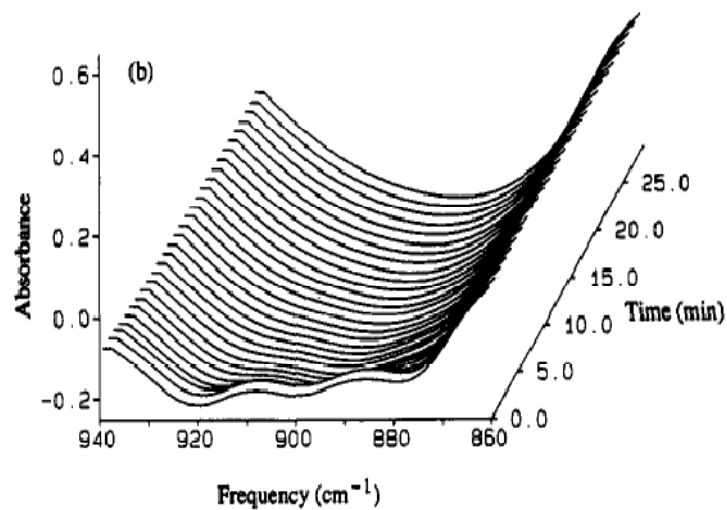
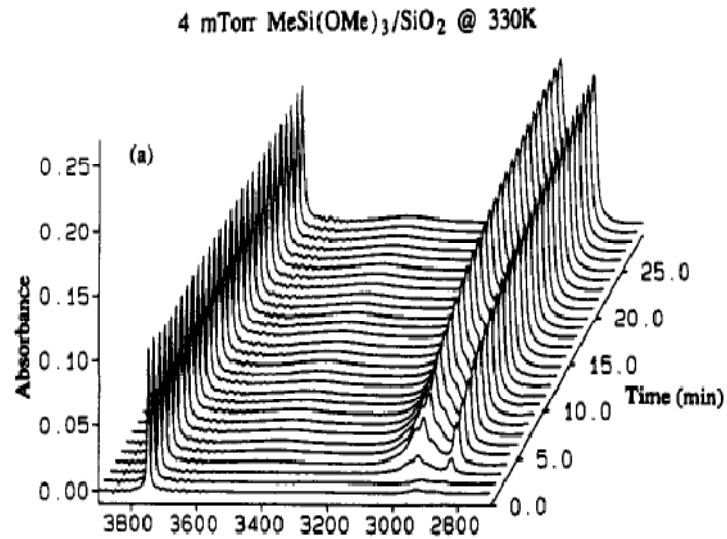
Morrow et Cod, J. Phys. Chem. 80 (1976) 1995, 1998, 2761 ;

Chuang et Maciel, J. Am. Chem. Soc. 118 (1996), J. Phys. Chem. B 101 (1997)

Ceresoli et al. Phys. Rev. Lett. 84 (2000) 3887

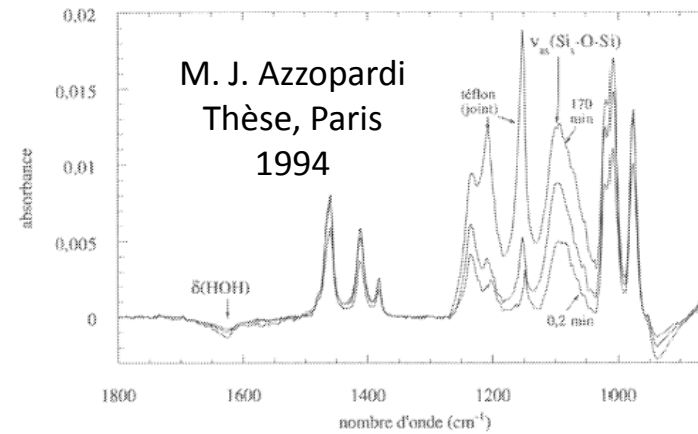
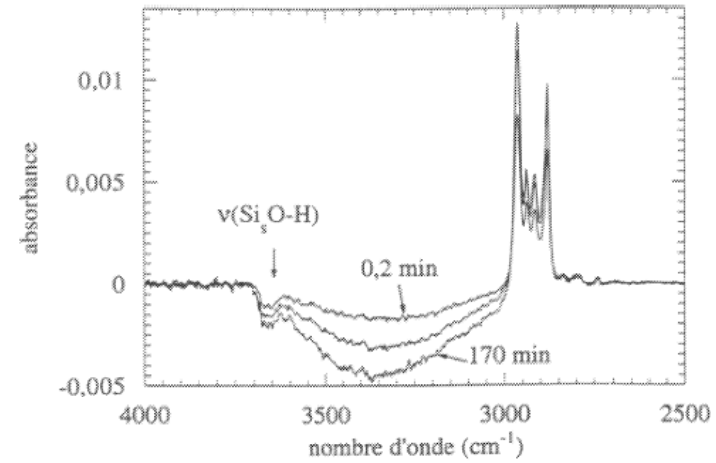
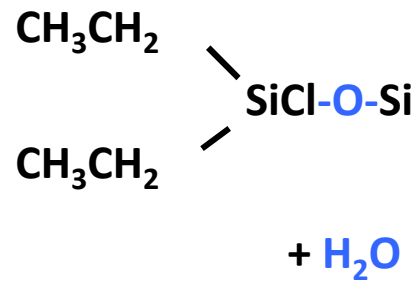
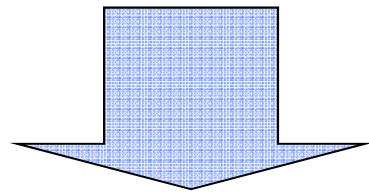
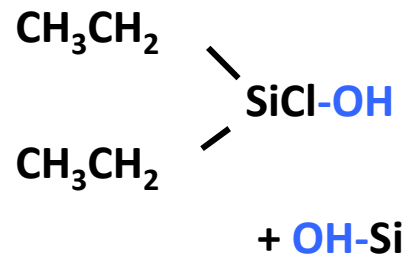
Roder et al. J. Chem. Phys. 114 (2001)

# Greffage par attaque nucléophile



Dubois et Zegarski, J. Phys. Chem. 97 (1993) 1665

# Silanols de surface





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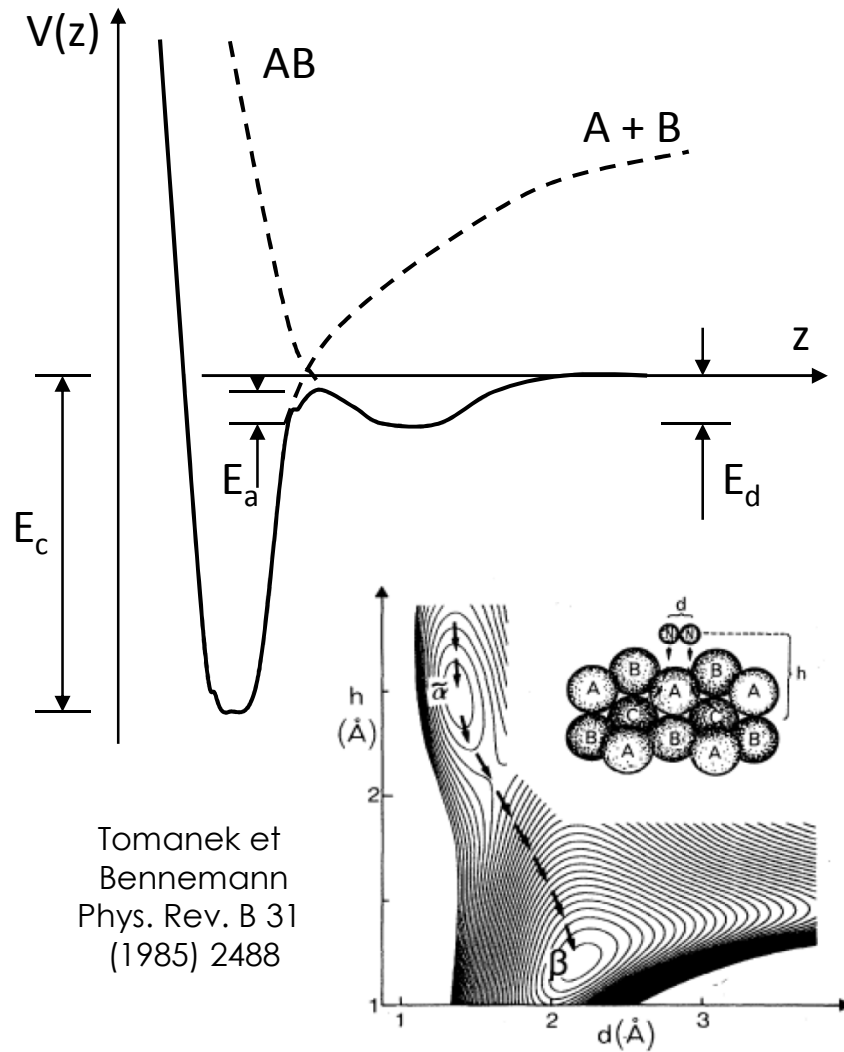
## Profil redox du verre flotté

le profil de l'étain

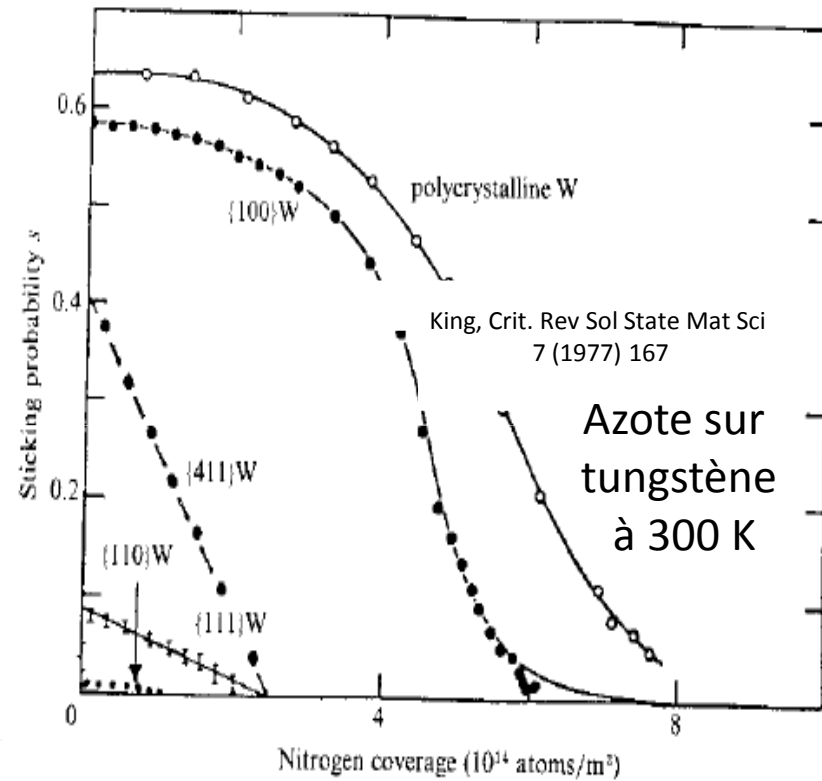
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# Représentation classique



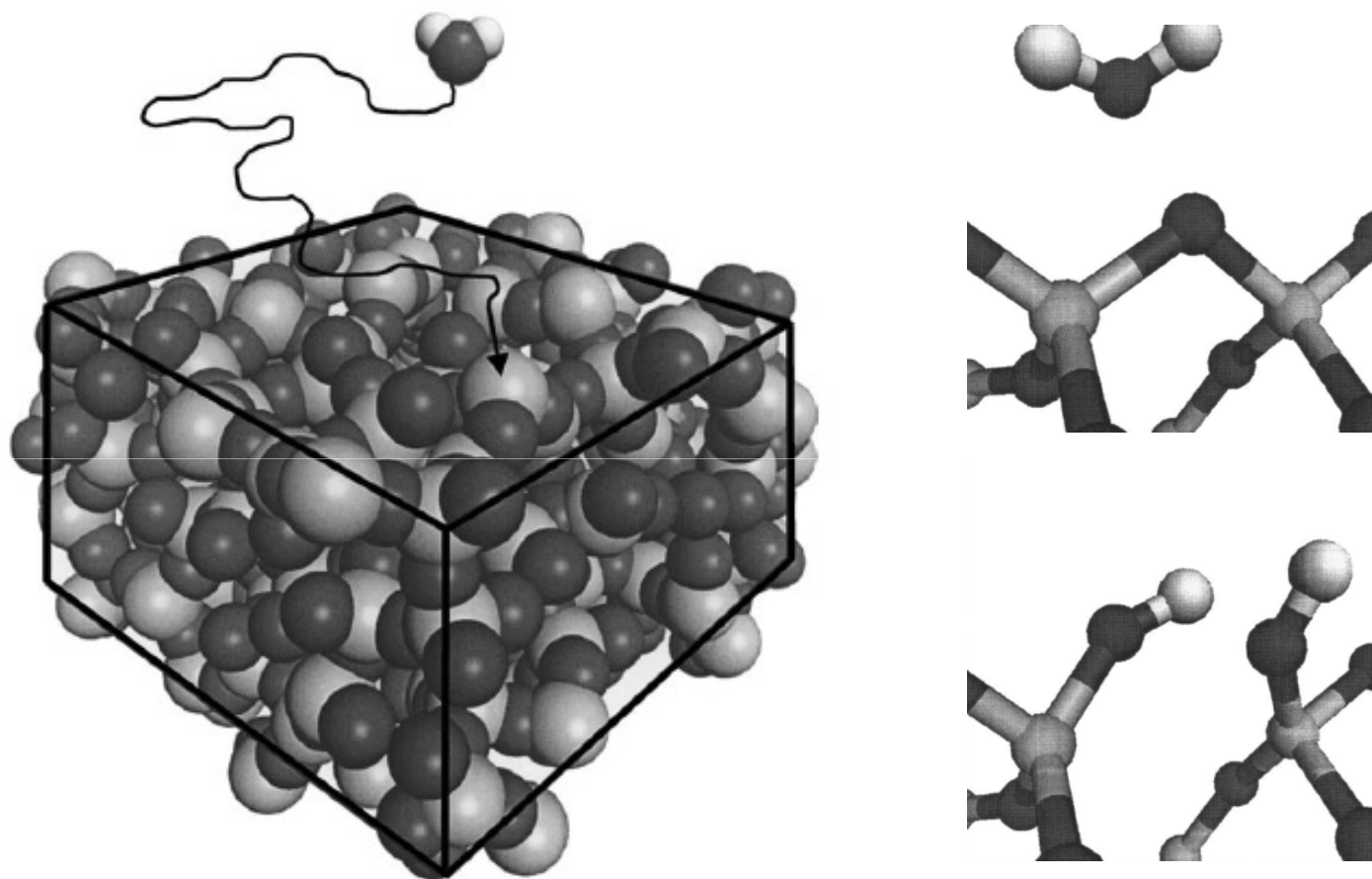
Tomanek et  
Bennemann  
Phys. Rev. B 31  
(1985) 2488



Azote sur  
tungstène  
à 300 K

Densité des faces du tungstène  
 $(110) > (100) > (111)$

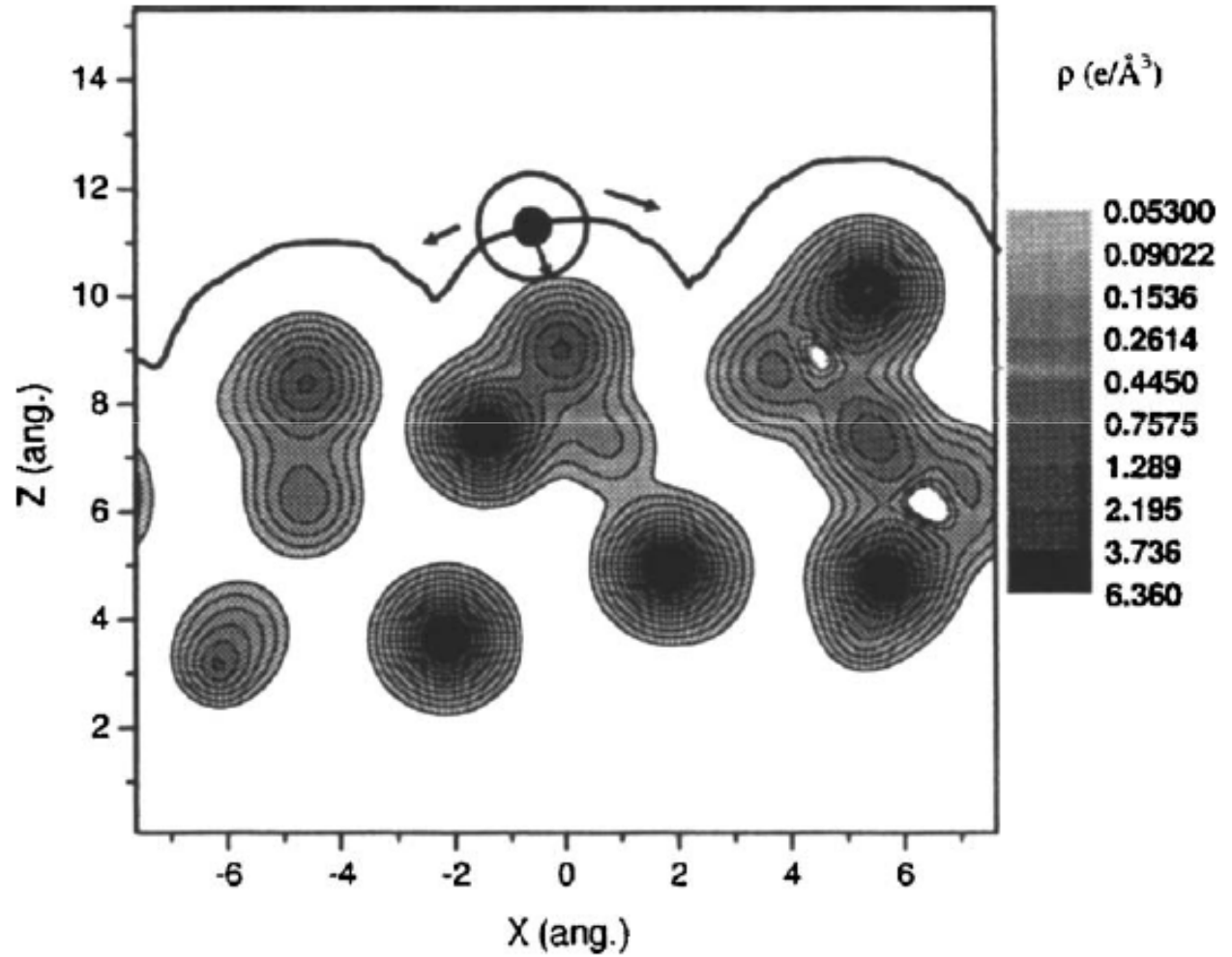
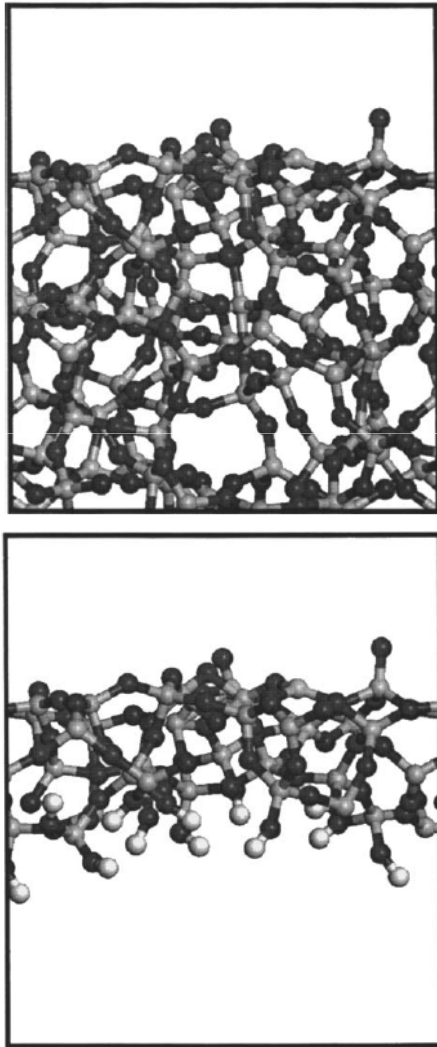
# Sites pertinents



E.A. Leed, C.G. Pantano, J. Non-Cryst. Solids 325 (2003) 48

E. A. Leed, J. O. Sofo et C. G. Pantano, Phys. Rev. B 72 (2005) 155427

# Surface active

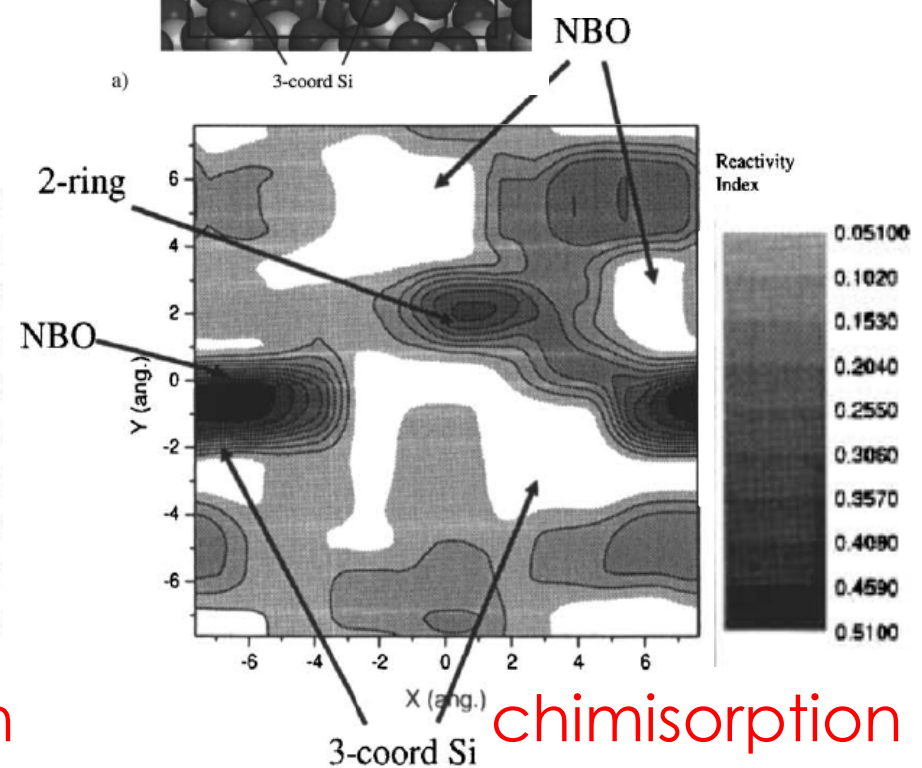
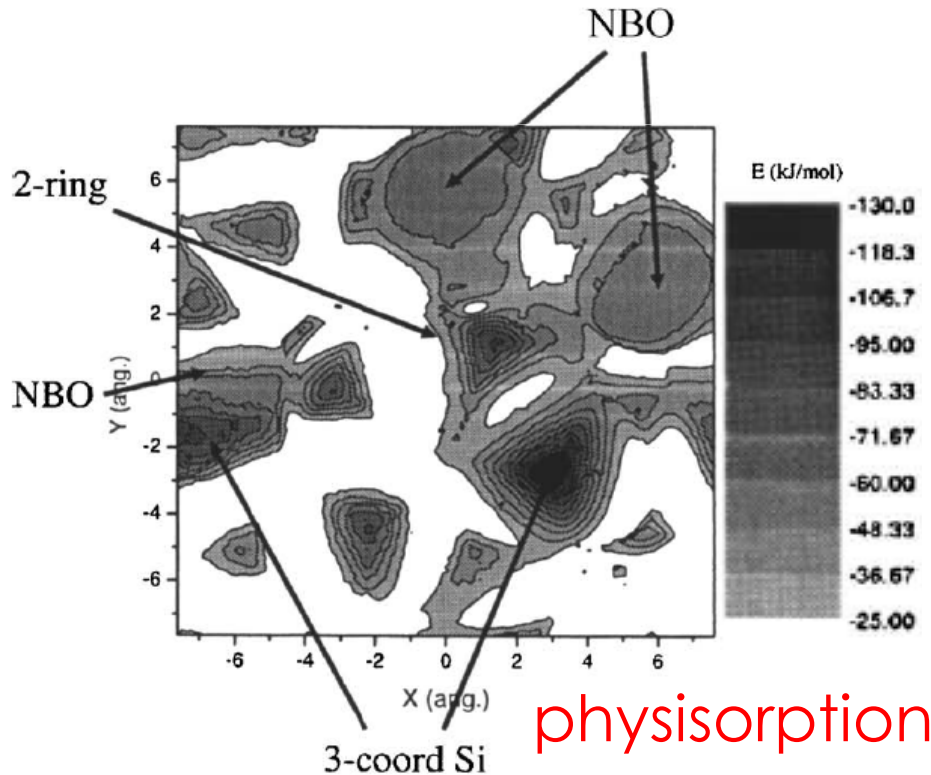
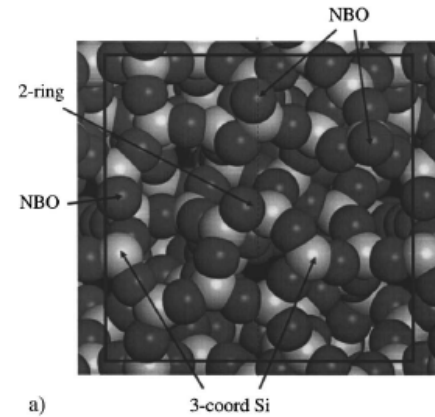


E. A. Leed, J. O. Sofo et C. G. Pantano, Phys. Rev. B 72 (2005) 155427

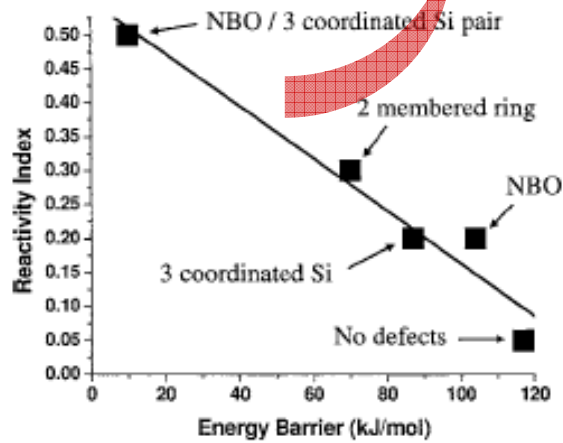
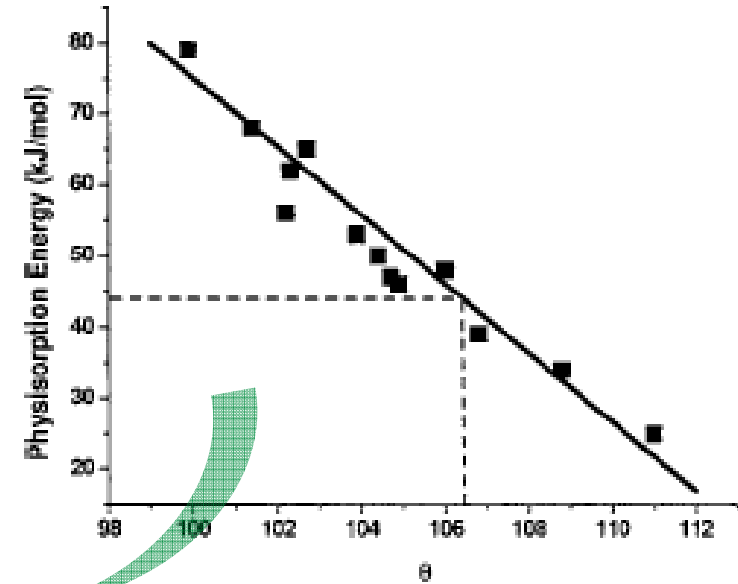
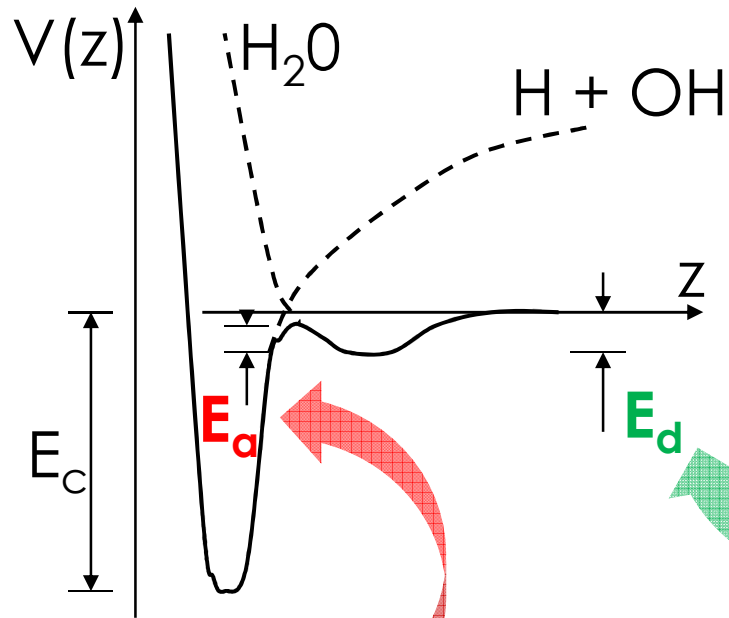
# Chimisorption vs physisorption

Physisorption (kJ.mol<sup>-1</sup>)

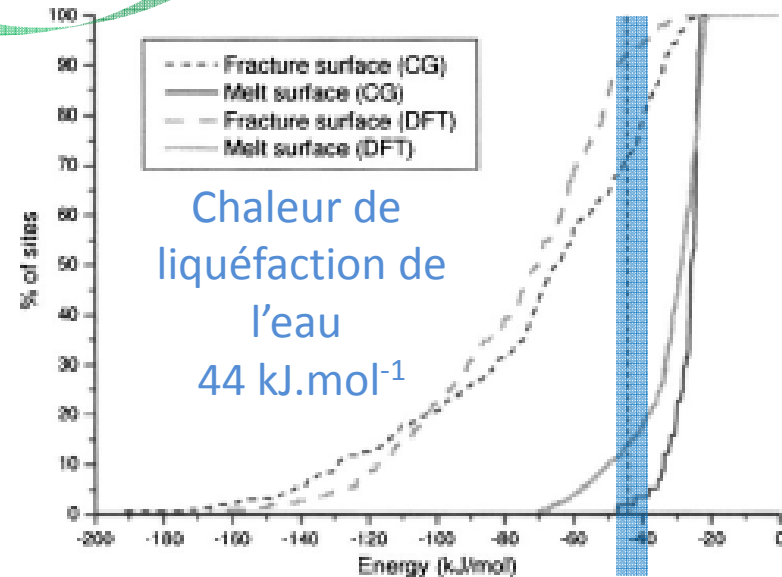
NBO	58
Si tri-coord	175
Face de tétraèdre	96



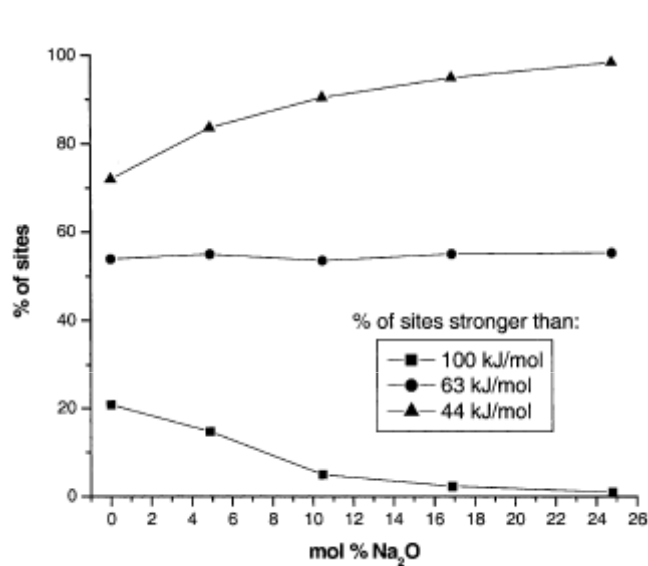
# Energies et taux de couverture



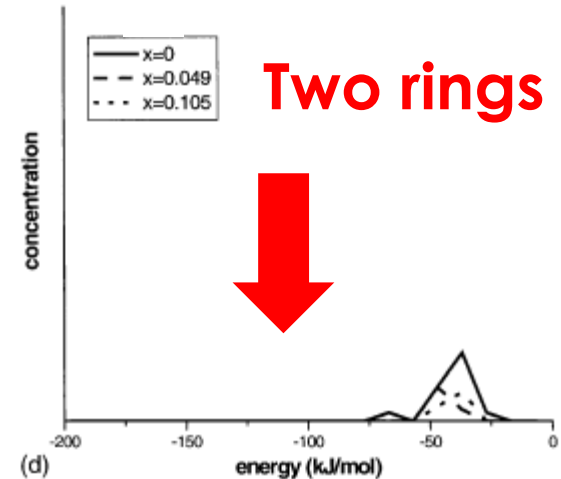
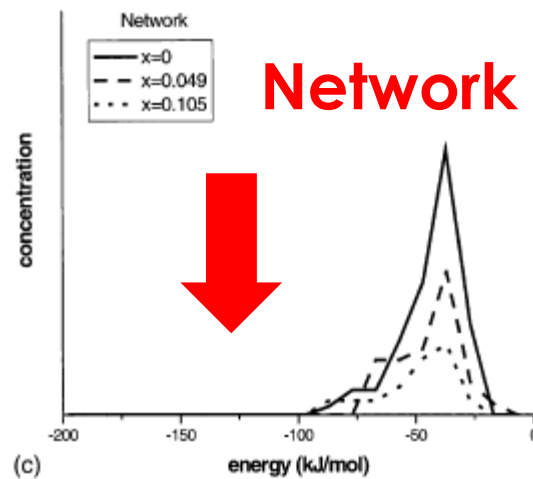
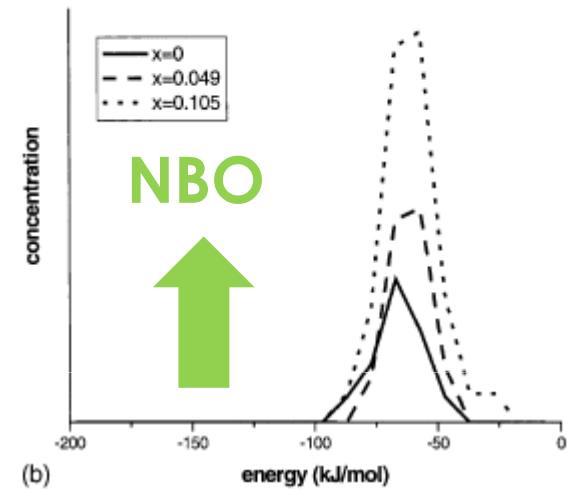
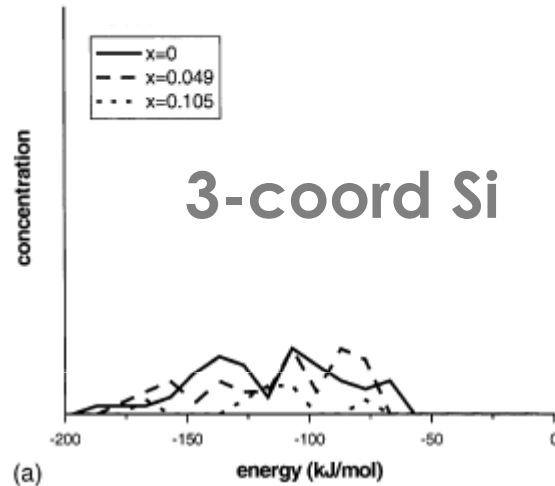
E. A. Leed et al.  
Phys. Rev. B 72  
(2005) 155427



# Effet des éléments alcalins sur la densité de sites actifs



E.A. Leed, C.G.Pantano  
 J. Non-Cryst. Solids  
 325 (2003) 48



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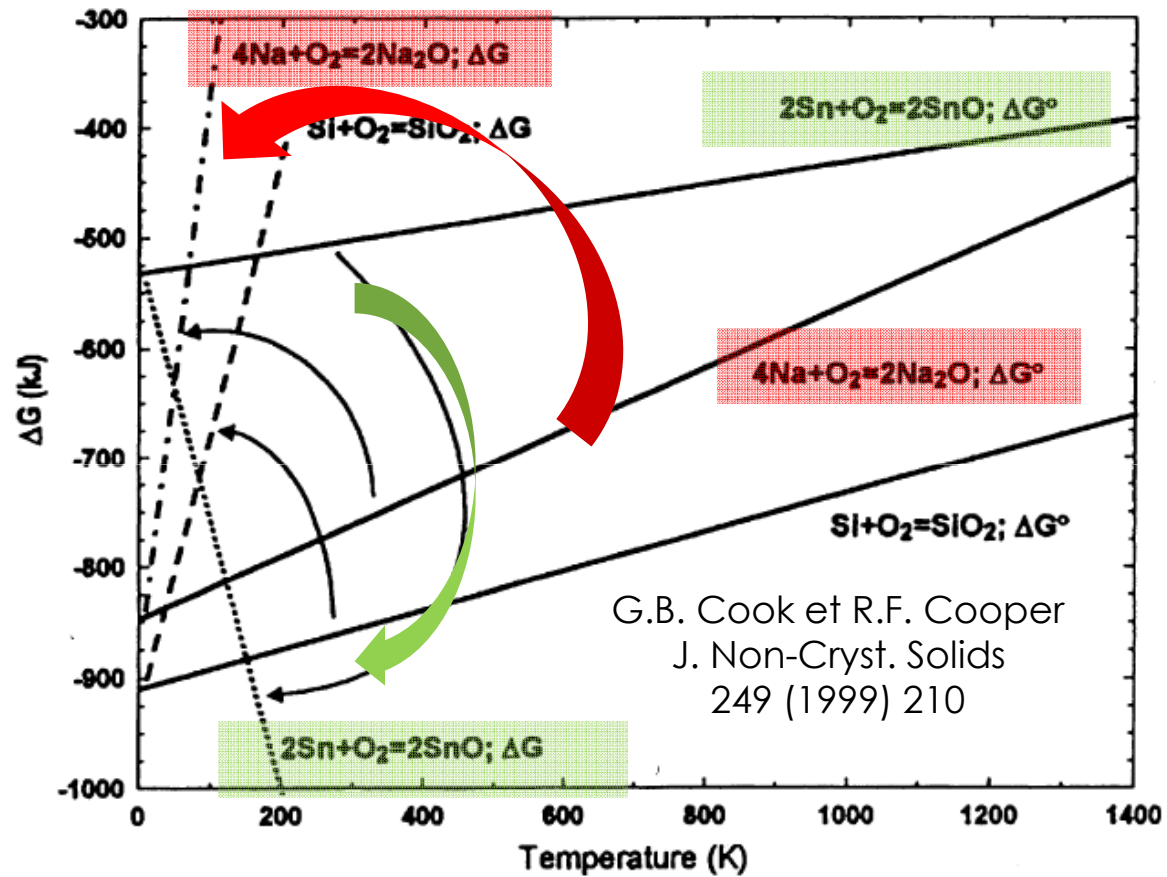
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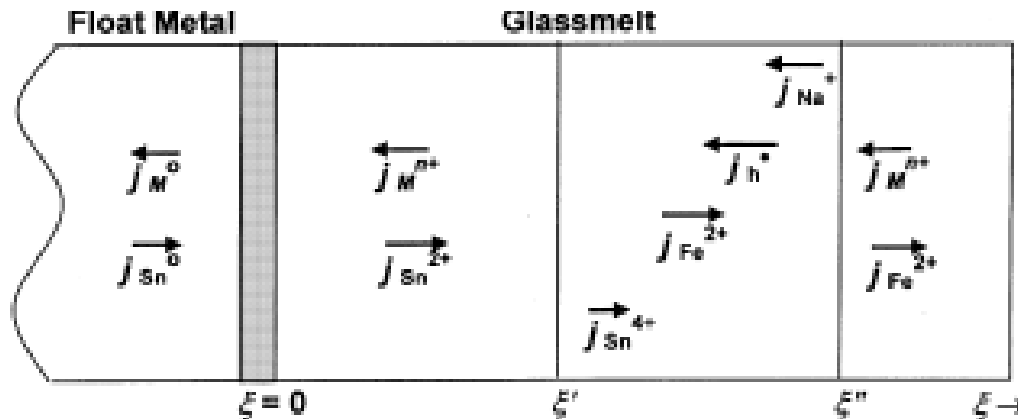
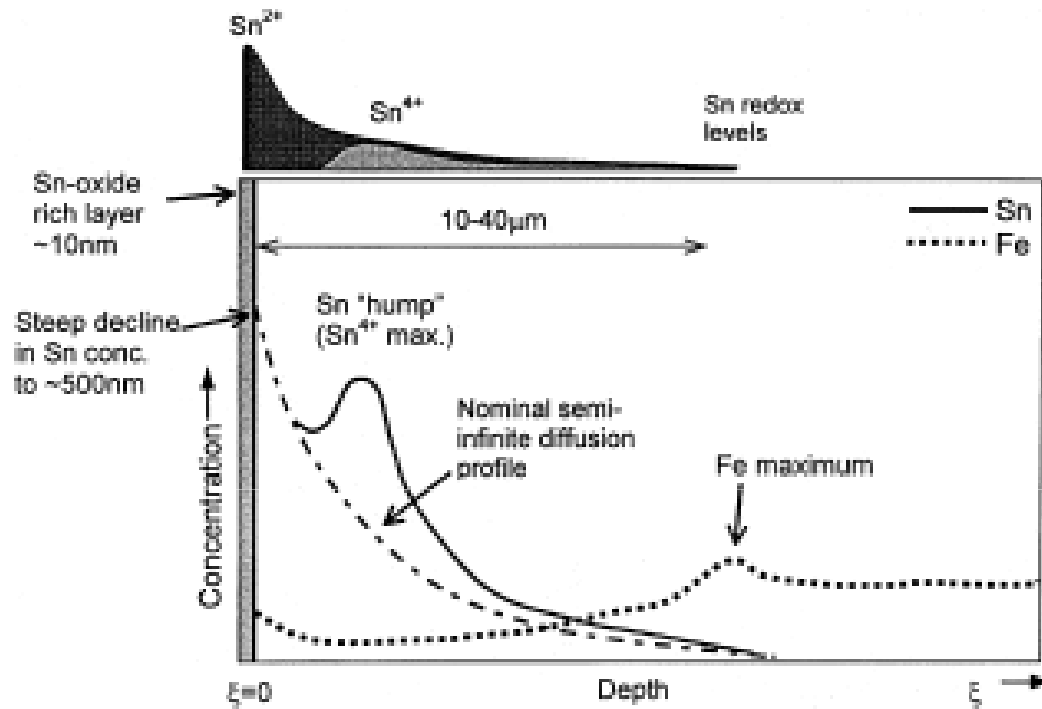
# Activités chimique au contact de l'étain



$$\Delta G_{Sn:SnO} = \Delta G_{Sn:SnO}^0 + RT \ln \frac{a_{SnO}^2}{a_{Sn}^2 p_{O_2}}$$

$$\Delta G_{Na:Na_2O} = \Delta G_{Na:Na_2O}^0 + RT \ln \frac{a_{Na_2O}^2}{a_{Na}^4 p_{O_2}}$$

# Profils de concentration



G.B. Cook et R.F. Cooper  
 J. Non-Cryst. Solids  
 249 (1999) 210

# Bloom

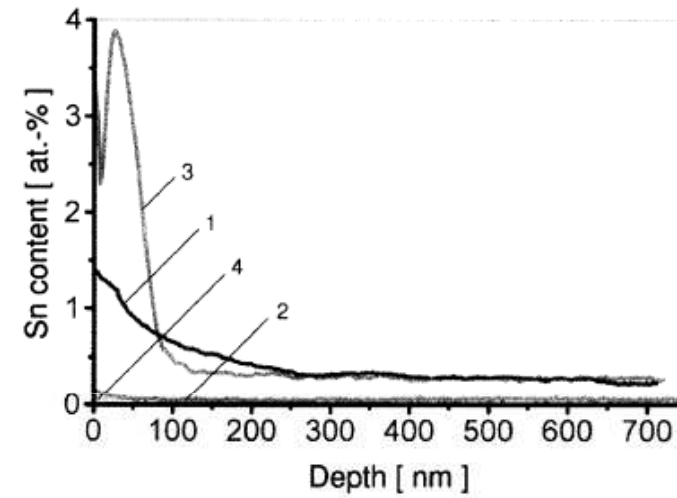
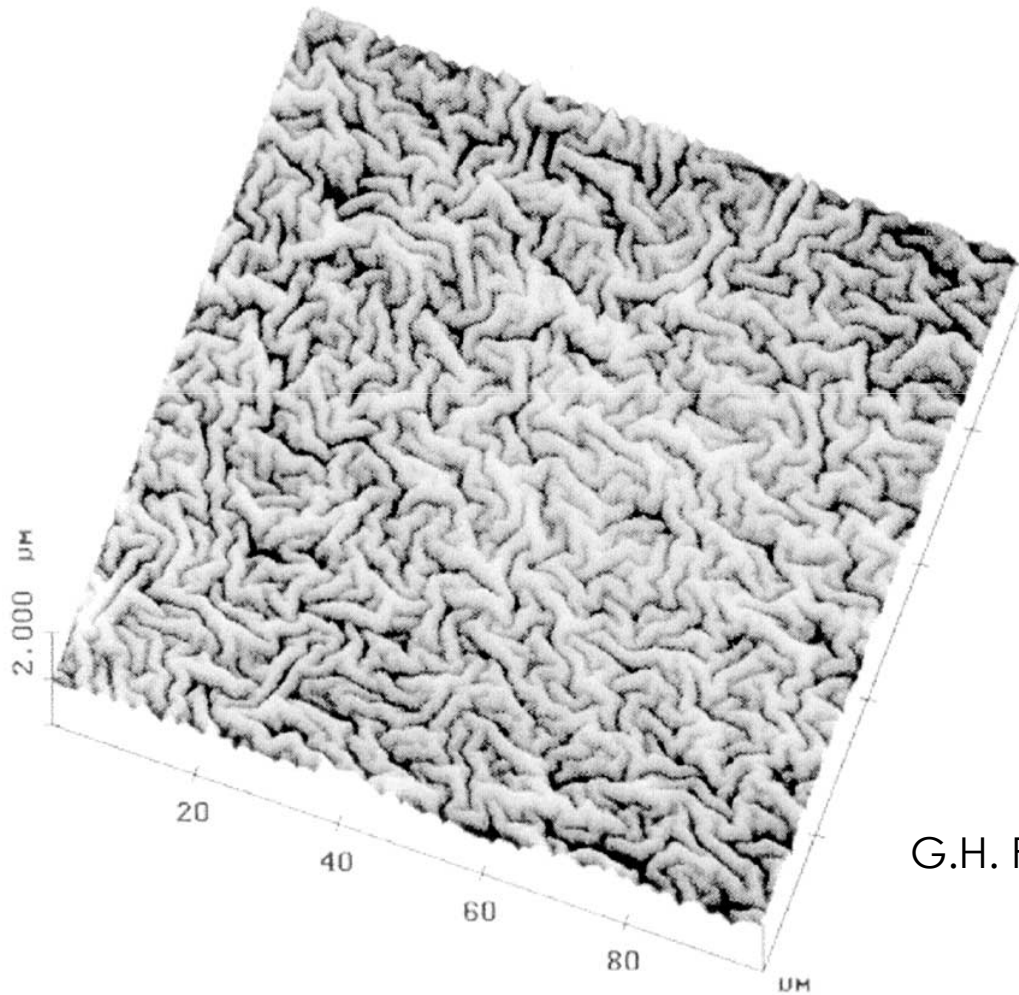


Fig. 5. SNMS tin in-depth profiles of two float glasses: curve 1,  $\text{Fe}_2\text{O}_3$  content 0.017 wt%, as-received; curve 2,  $\text{Fe}_2\text{O}_3$  content 1.80 wt%, as-received; curve 3,  $\text{Fe}_2\text{O}_3$  content 0.017 wt%, 1 h at 650 °C; curve 4,  $\text{Fe}_2\text{O}_3$  content 1.80 wt%, 1 h at 650 °C.

G.H. Frischat, C. R. Chimie 5 (2002) 759–763

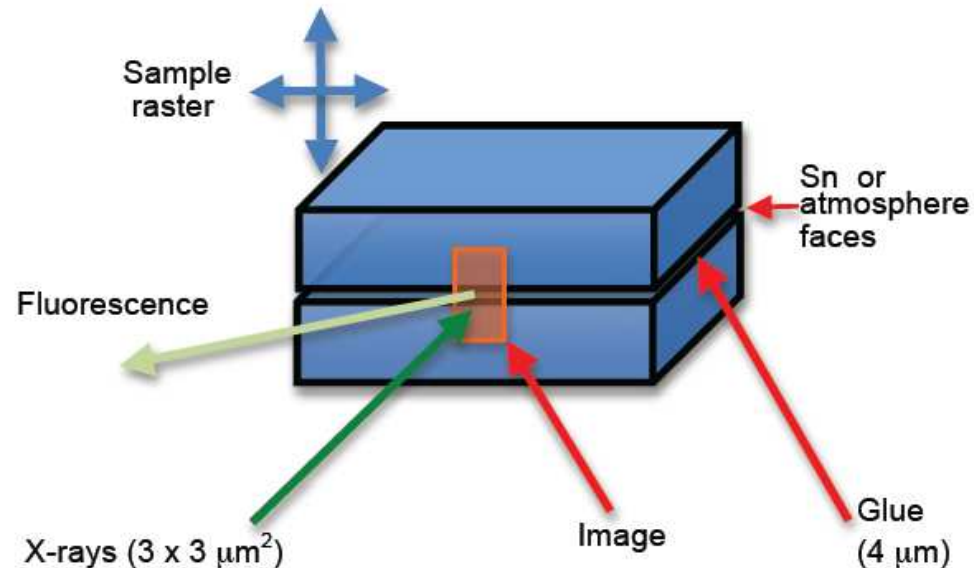
# Expériences

Expériences sur la ligne "LUCIA" (Ligne Utilisée pour la Caractérisation par Imagerie et Absorption – SOLEIL)

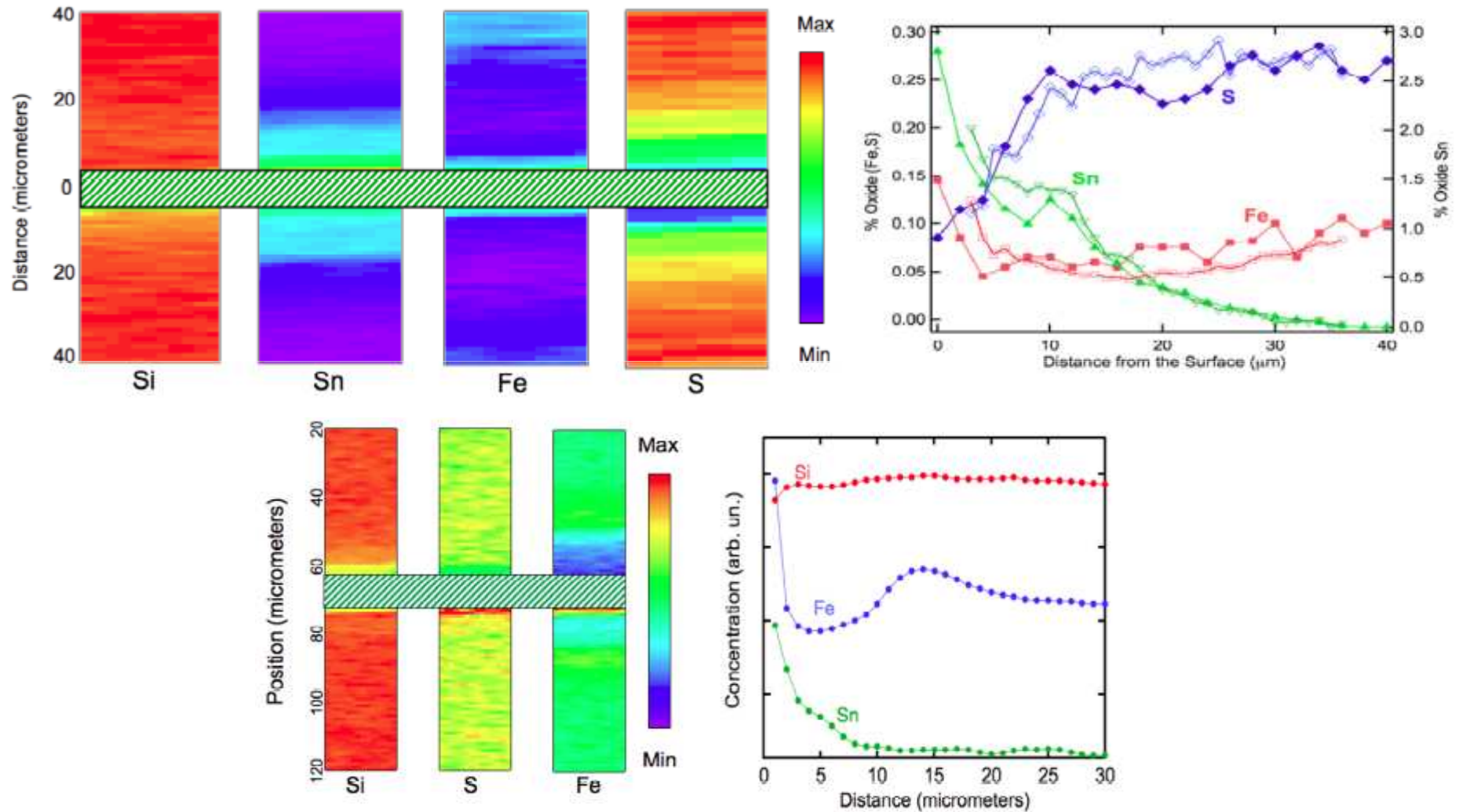
Responsables de ligne : Anne-Marie Flank et Pierre Lagarde)

- micro-absorption X ( $\mu$ XAS) et micro-fluorescence ( $\mu$ XRF) dans le domaine des rayons X dits "tendres" (0.8-8 keV)
- cartographies élémentaires à l'échelle du spot de photons ( $2 \times 2 \mu\text{m}^2$ )

Collaboration Anne-Marie Flank et Pierre Lagarde

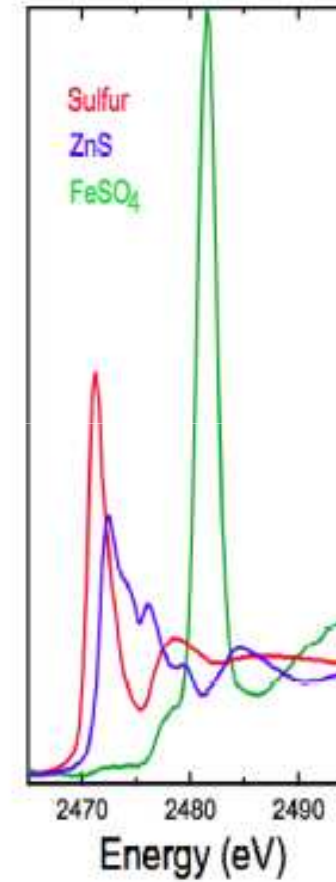
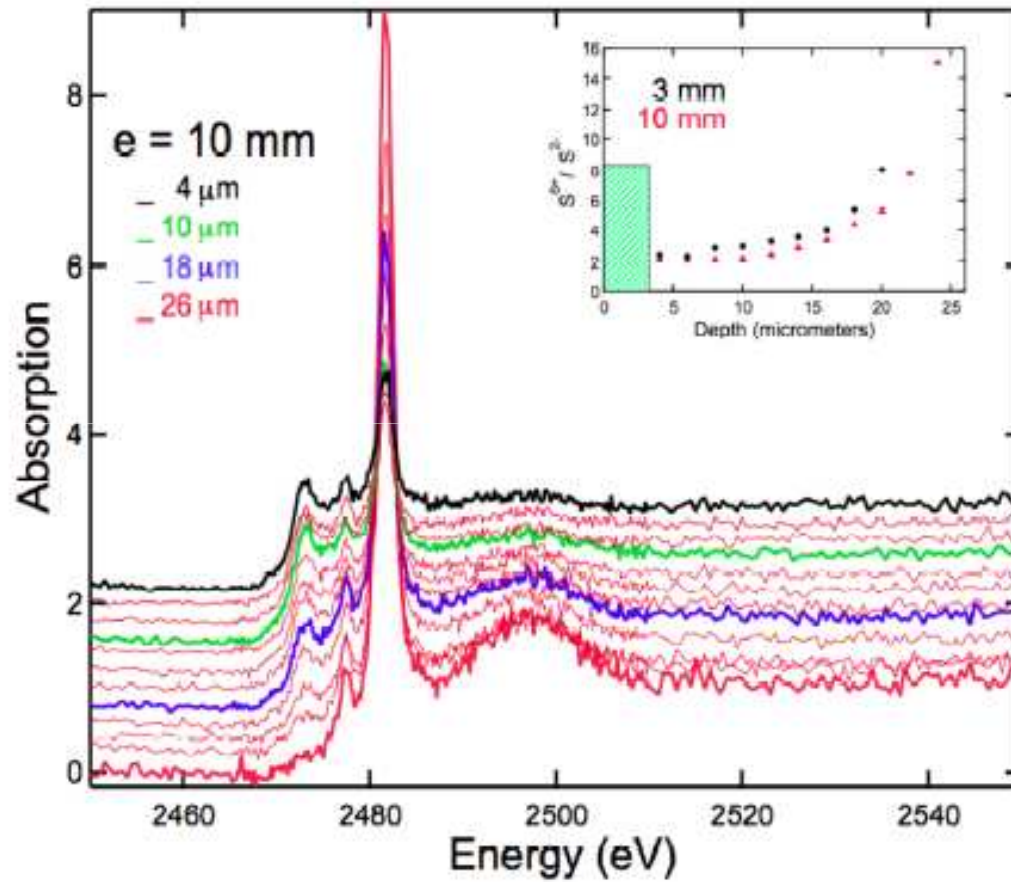


# Microscopie XAS et microsonde

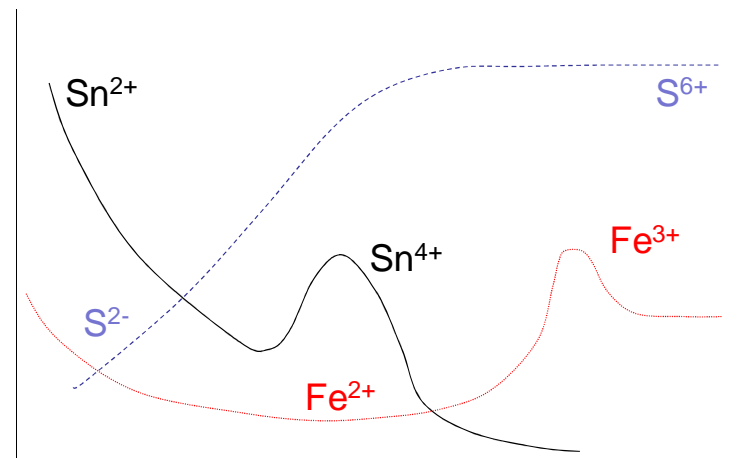
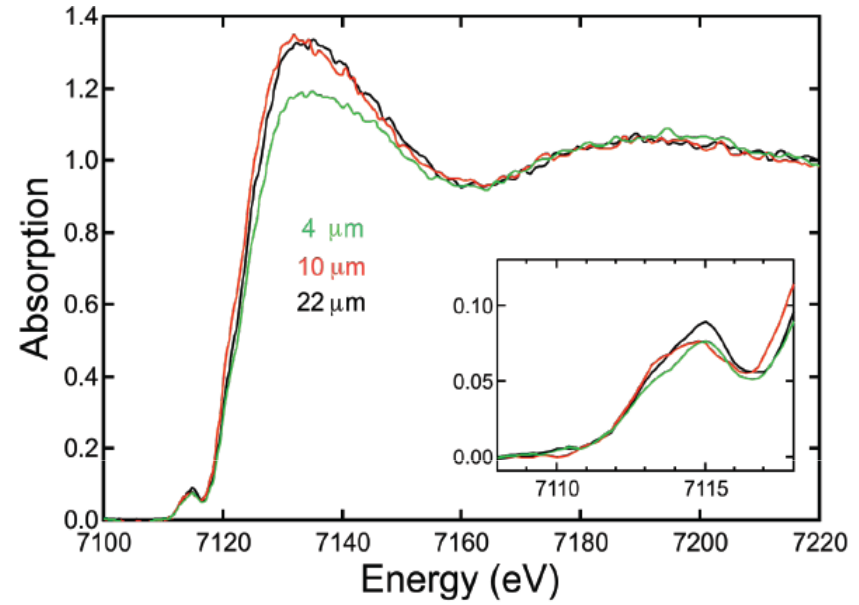
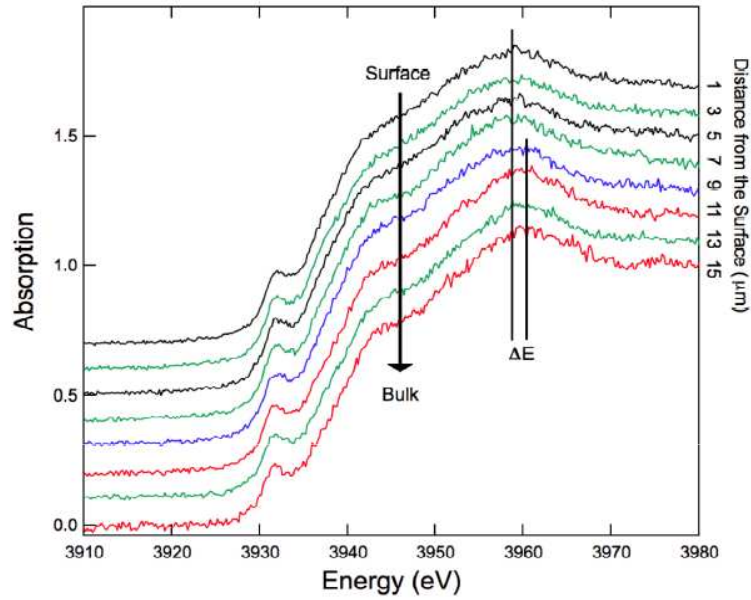


Anne-Marie, Flank, Pierre Lagarde, Hervé Montigaud, JJ, en préparation

# Profil du soufre



# Profil redox



## Remerciements

Anne-Marie Flank  
Pierre Lagarde

Hervé Montigaud  
Marie-Hélène Chopinet  
Patrick Garnier