Diffusion dans les verres et liquides

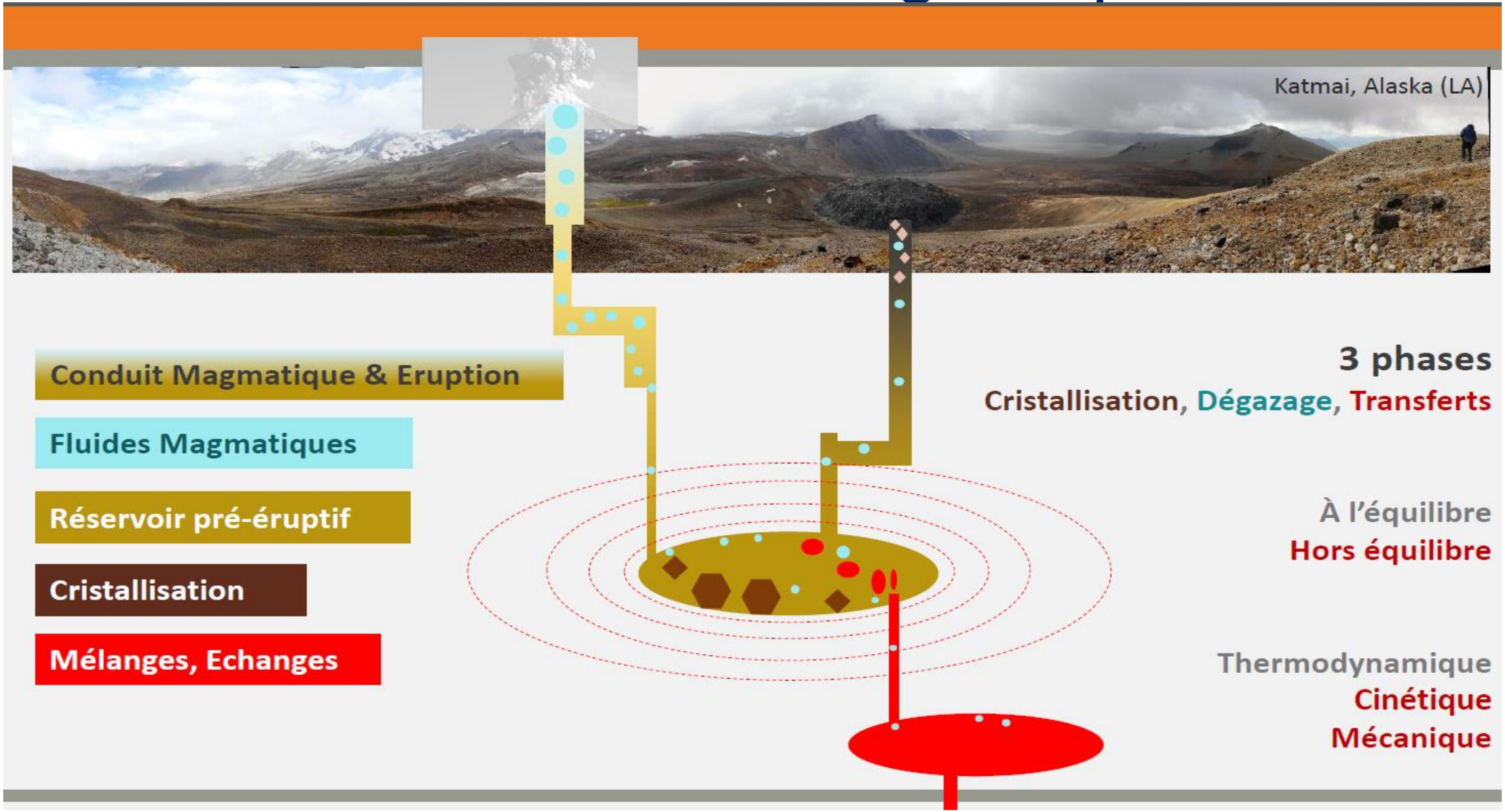
Quelques illustrations en science de la Terre

Earth Sciences Institute of Orléans

ISTO

Equipe Magma

La Plomberie Magmatique



3 phases

Cristallisation, Dégazage, Transferts

À l'équilibre

Hors équilibre

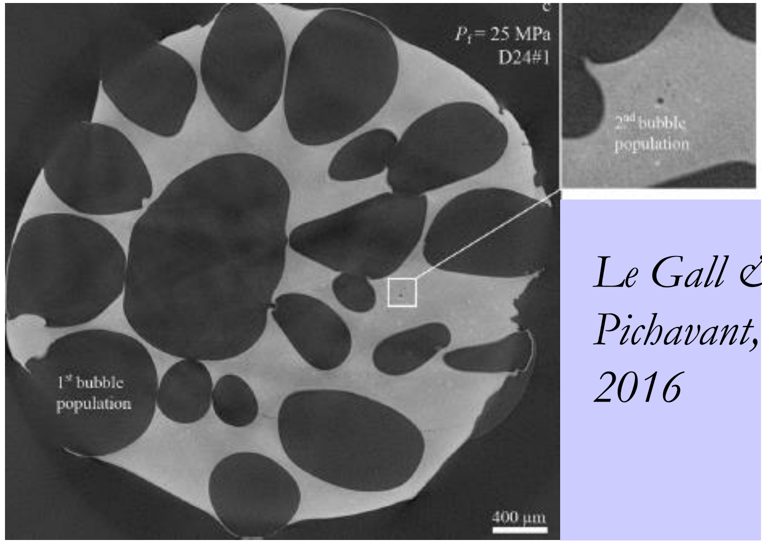
Thermodynamique

Cinétique

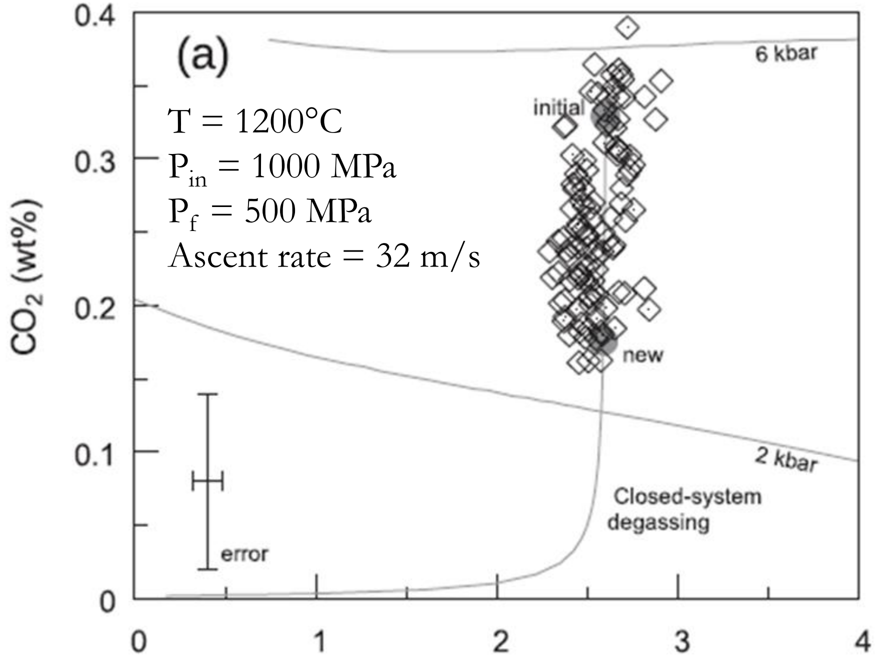
Mécanique

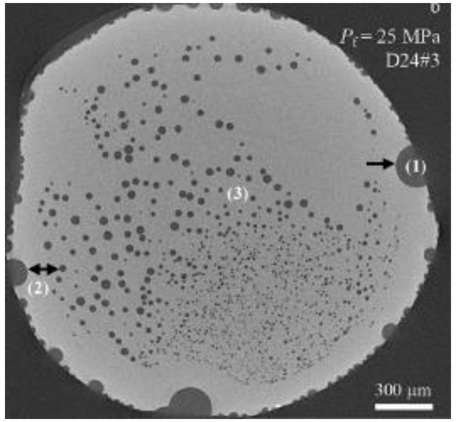
Mobilités différentielles de H_2O et CO_2 dans les magmas

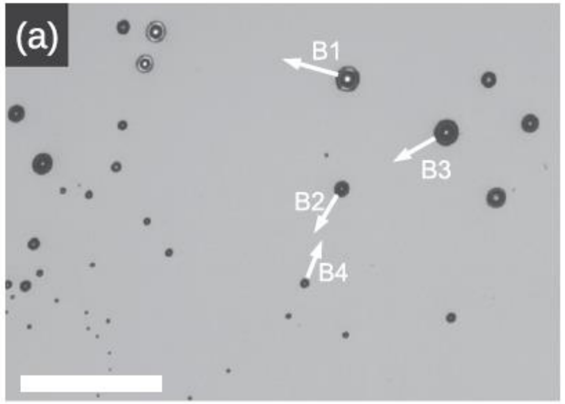
Croissance des bulles

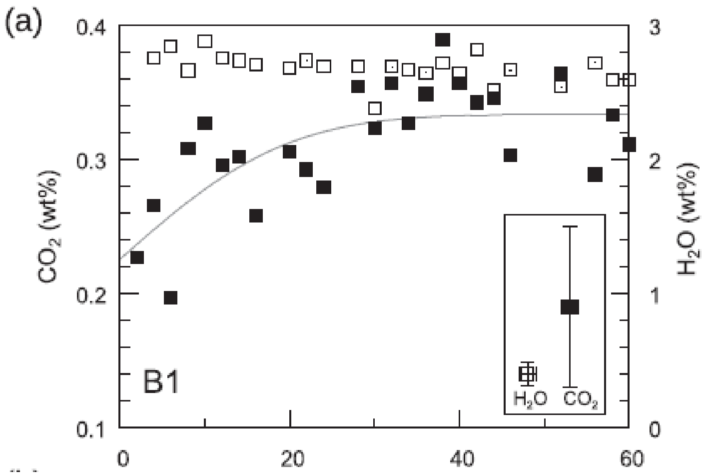


Le Gall & Pichavant, 2016









Nucléation des bulles

Yoshimura, 2015

REDOX ET DIFFUSION

Earth Sciences Institute of Orléans

ISTO

Bayerisches Geoinstitut

Bayerisches Forschungsinstitut für Experimentelle Geochemie und Geophysik Universität Bayreuth

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Geochimica et Cosmochimica Acta 74 (2010) 1653–1671

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Time-dependent changes of the electrical conductivity of basaltic melts with redox state

A. Pommier[a,*], F. Gaillard[b], M. Pichavant[b]

Pergamon

Geochimica et Cosmochimica Acta, Vol. 67, No. 13, pp. 2427–2441, 2003

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Rate of hydrogen–iron redox exchange in silicate melts and glasses

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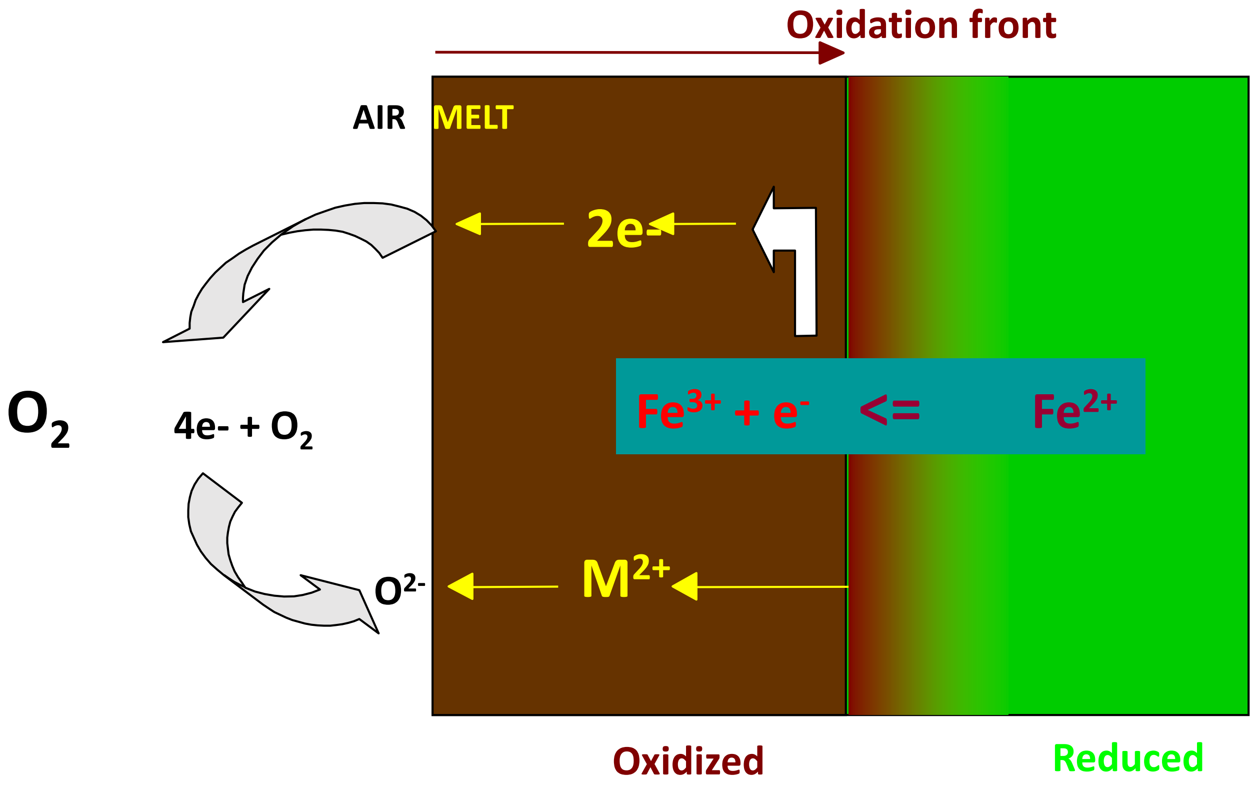
American Mineralogist, *Volume 88, pages 308–315, 2003*

Chemical transfer during redox exchanges between H_2 and Fe-bearing silicate melts

FABRICE GAILLARD,[1,*] MICHEL PICHAVANT,[1] STEPHEN MACKWELL,[2] RÉMI CHAMPALLIER,[1]
BRUNO SCAILLET,[1] AND CATHERINE MCCAMMON[2]

Cooper and Co-workers (1996…):

Mechanisms and Rate of Basalt Oxidation in Anhydrous System: A diffusion-limited process



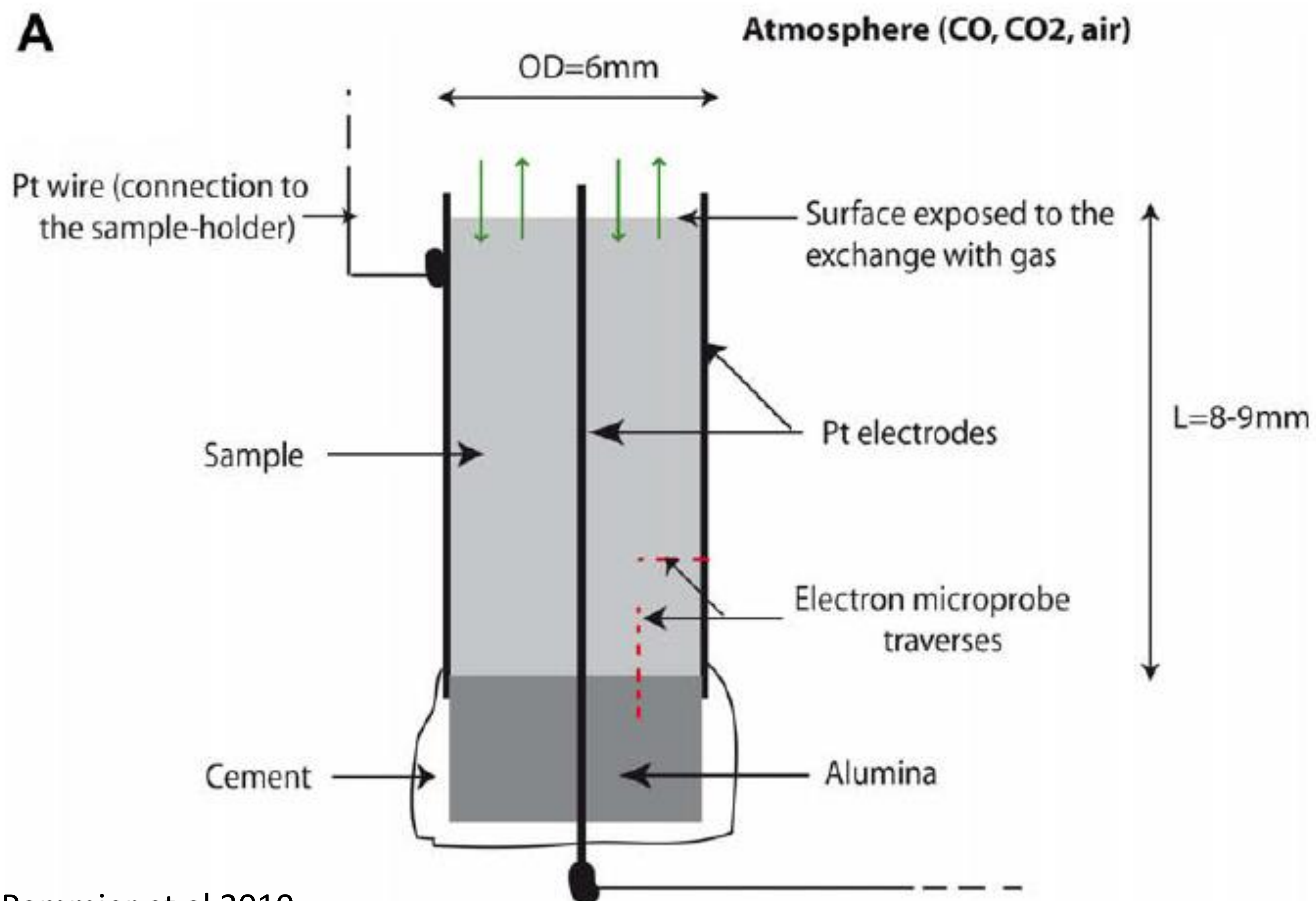
$O_2 + 4\,e^- \Rightarrow 2\,O^{2-}$

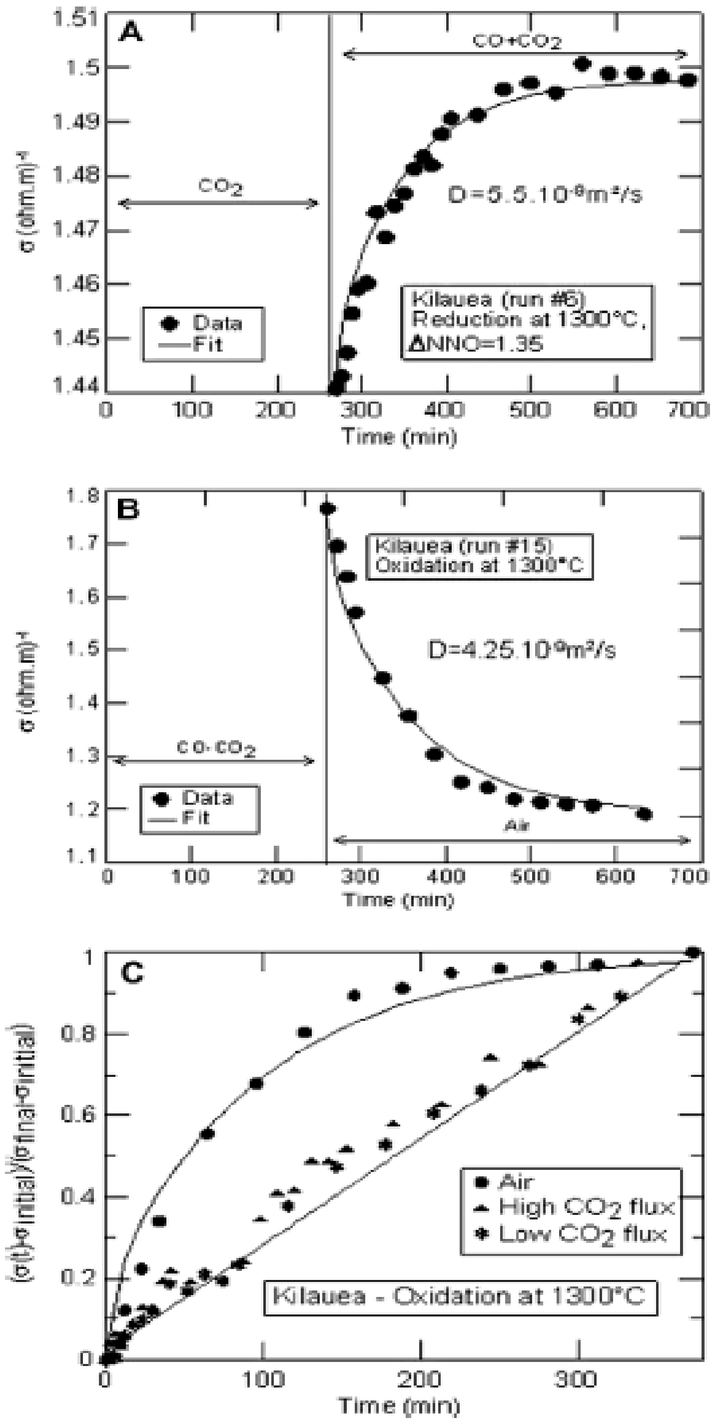
$Fe^{2+} \Rightarrow Fe^{3+} + e^-$

⇒ Oxidation rate not limited by O incorporation but by divalent cation or electron migration rates

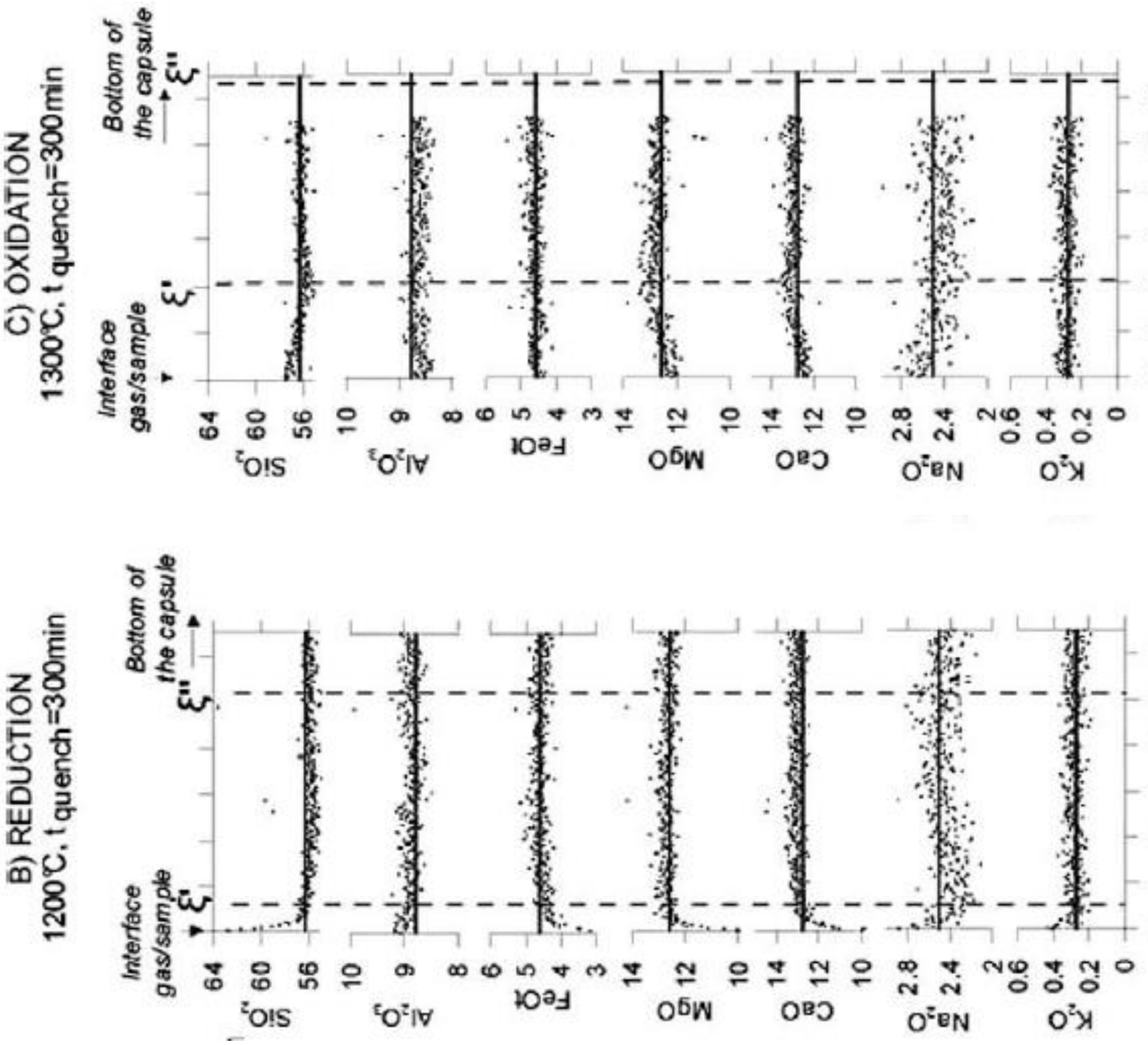
⇒ However, a model challenged in 2010 & only applicable for dry systems (Hydrogen-free)

$$\frac{\sigma(t)-\sigma_{\text{initial}}}{\sigma_{\text{equilibrium}}-\sigma_{\text{initial}}}=1-\sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}.\exp\left[\frac{-D(2n+1)^2\pi^2 t}{4L^2}\right]$$



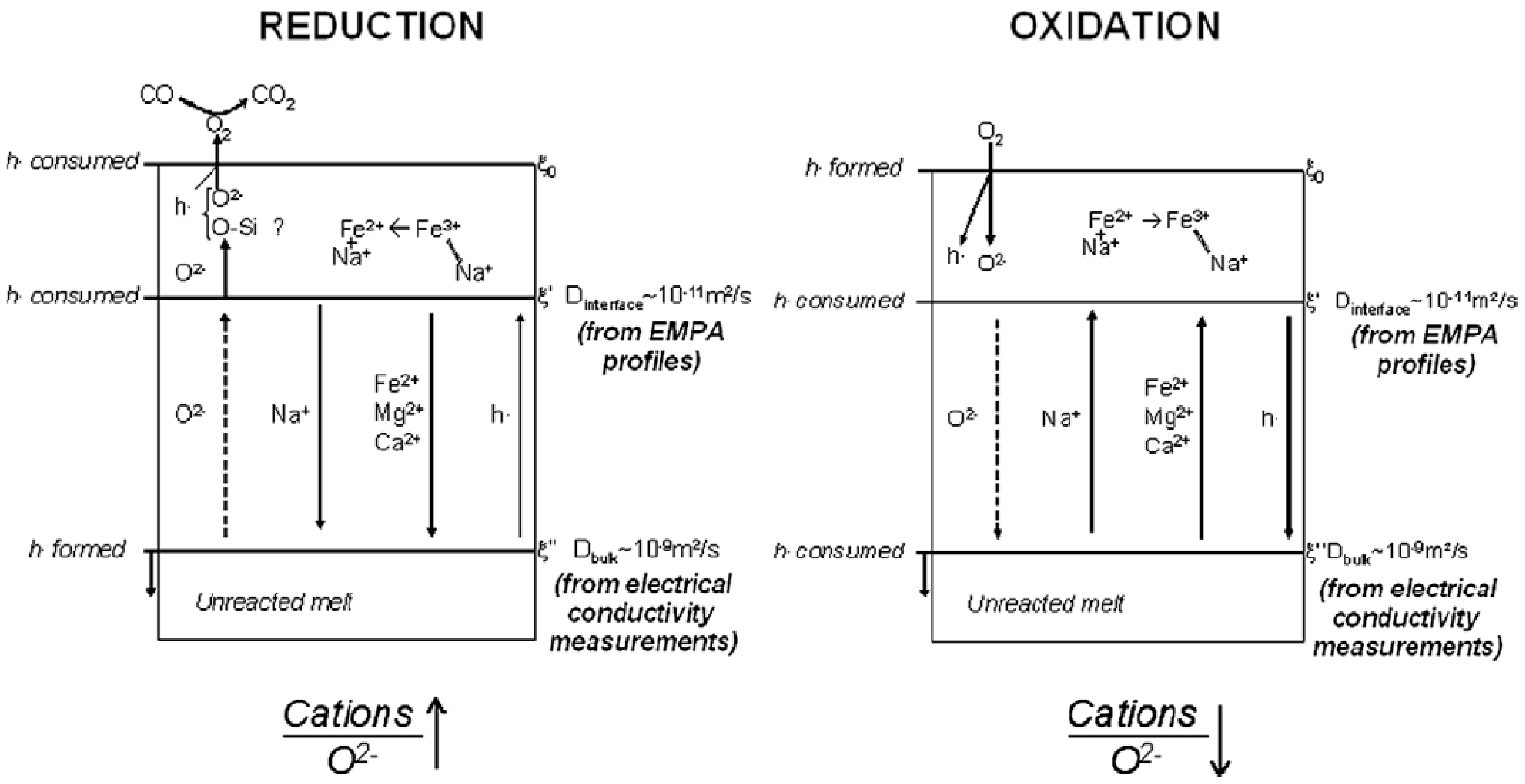


Pommier et al 2010



2 fronts de diffusion?

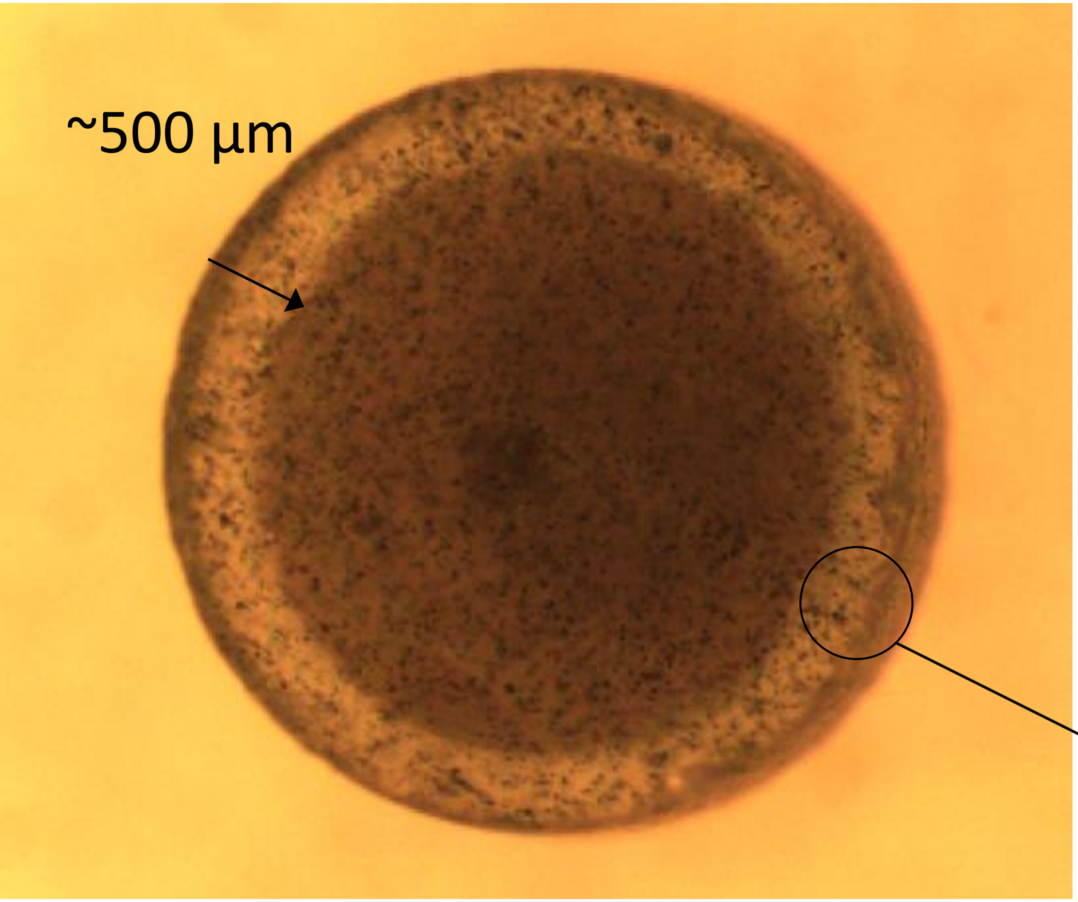
DIFFUSION D'OXYGENE AUSSI?



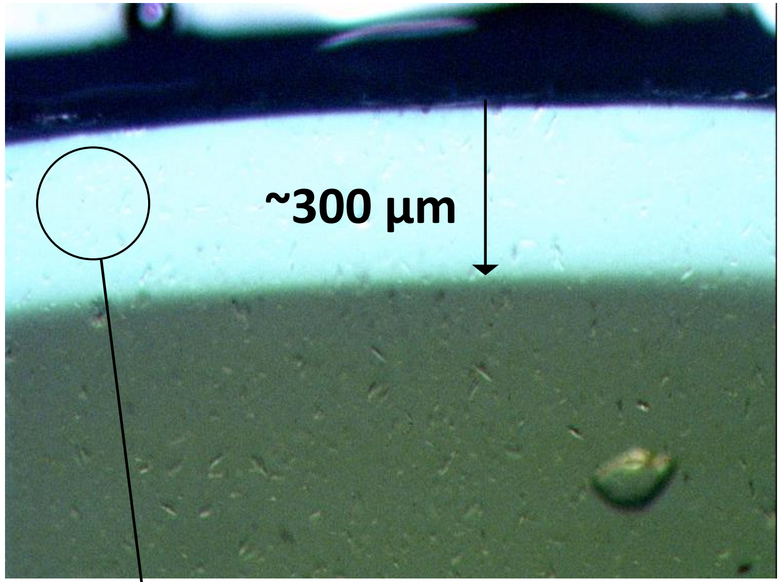
Reduction of Fe^{3+} by H_2: Glasses color and Fe^{3+}/Fe^{2+}

800°C, f_{H2} ~ 40 bar

Fe_2O_3 initial = 0.4 wt%, 5 min



Fe_2O_3 initial = 1.2 wt%, 30 min

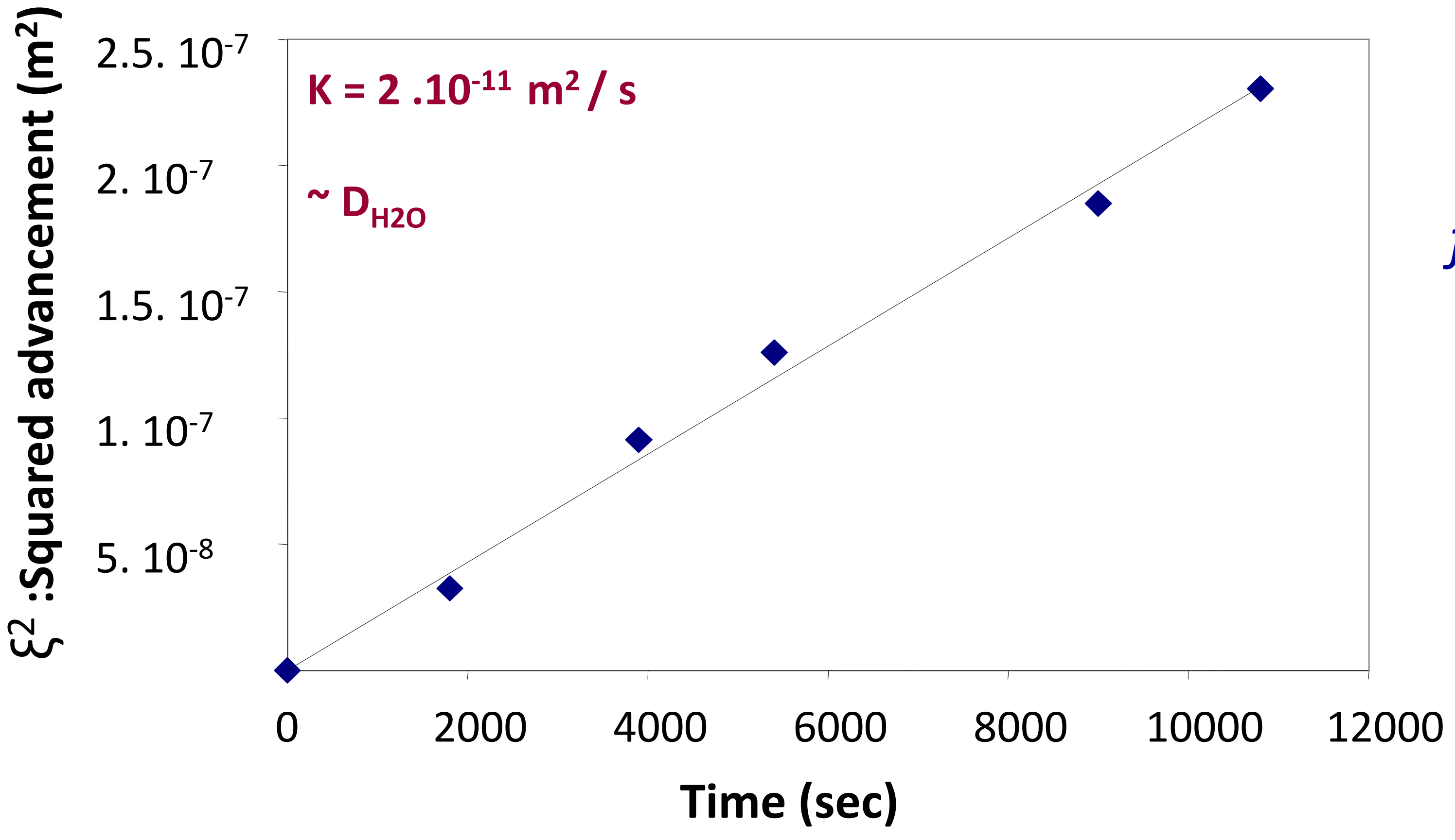


No Ferric iron measurable

Reduction of Fe^{3+} by H_2: Evidence for a diffusion-limited process

$\xi^2 = K.\ t$

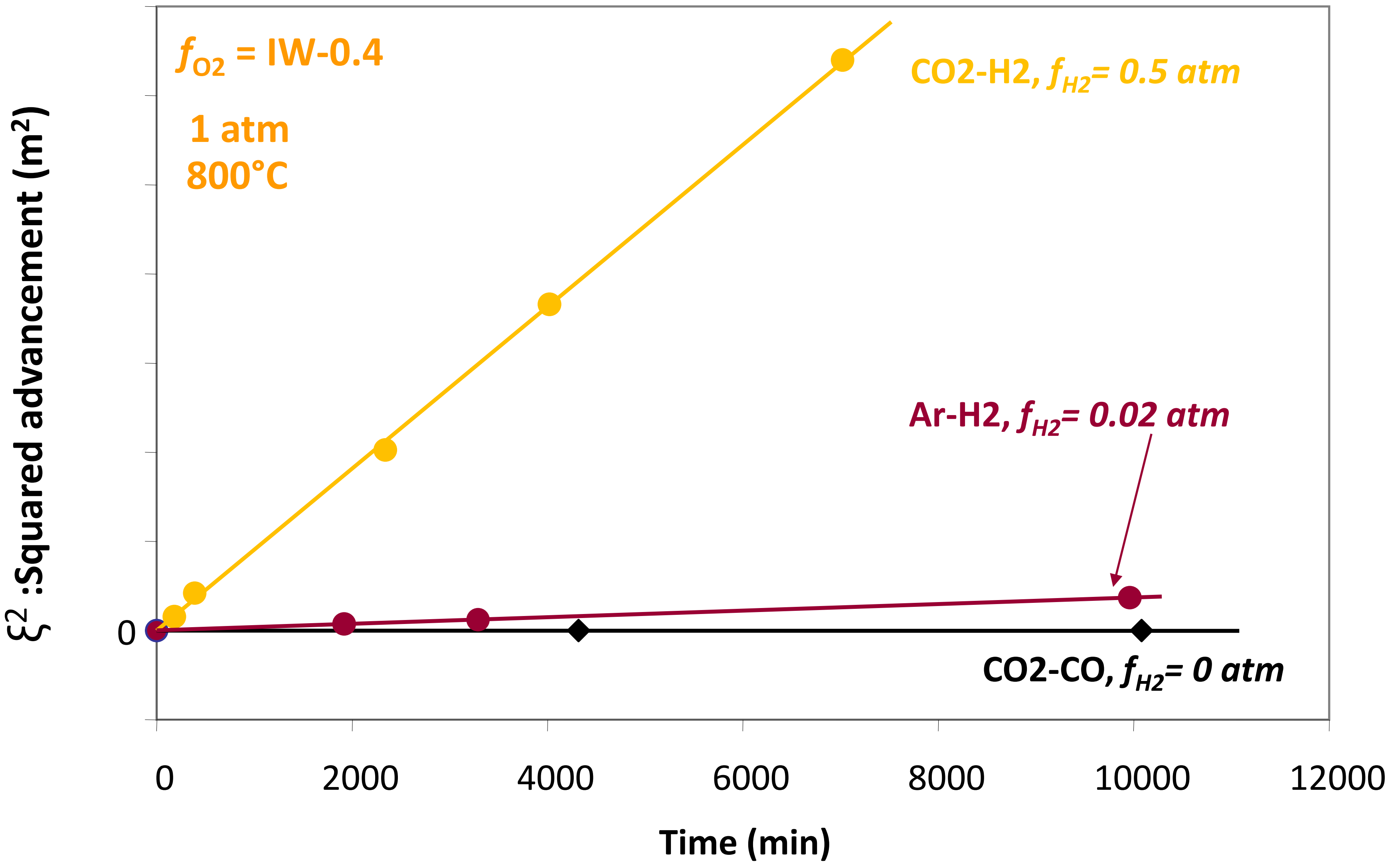
with K, function of D_x



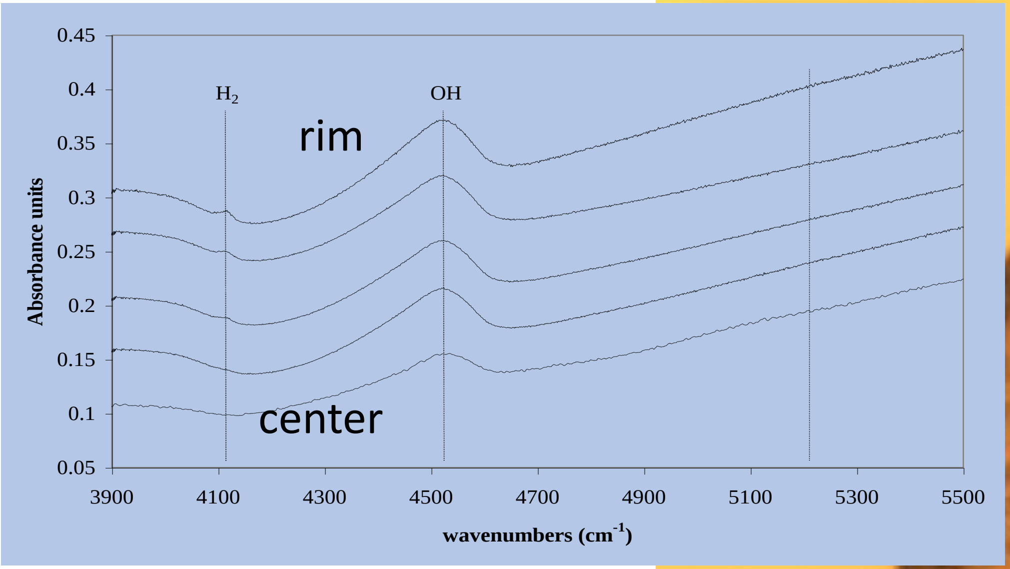
800°C

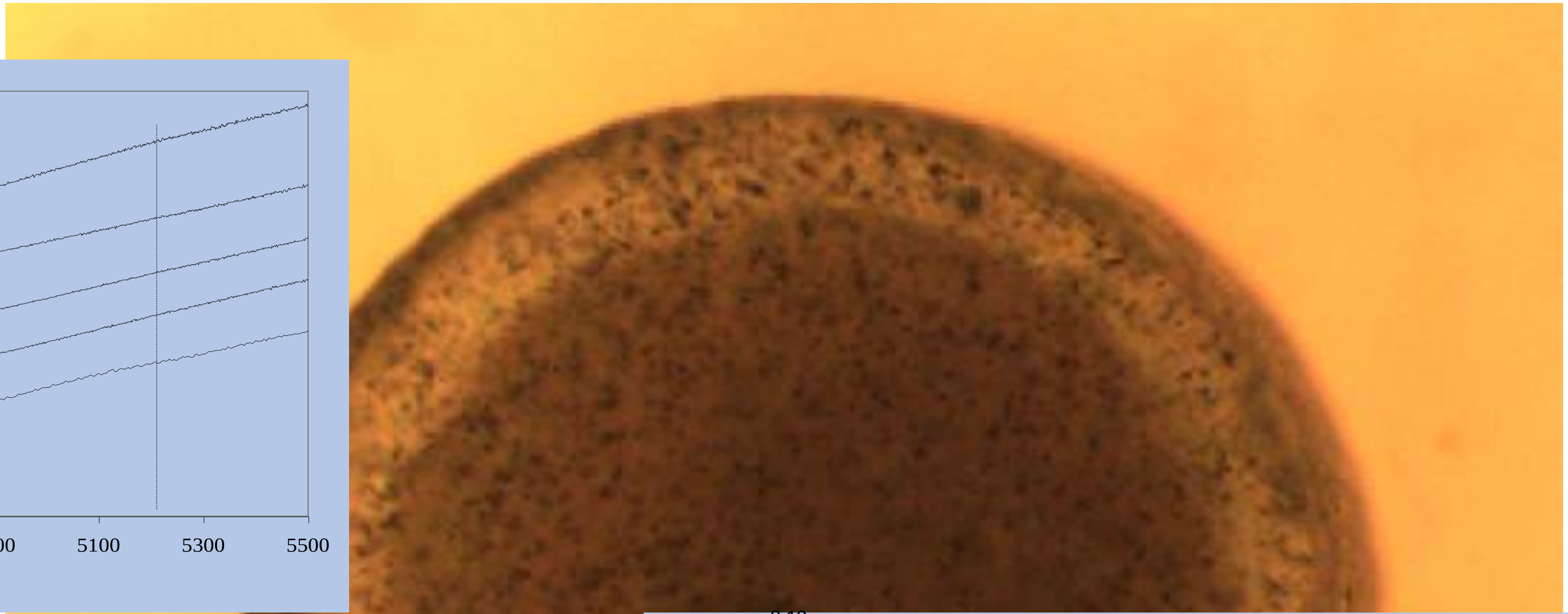
f_{H2} = 40 bar

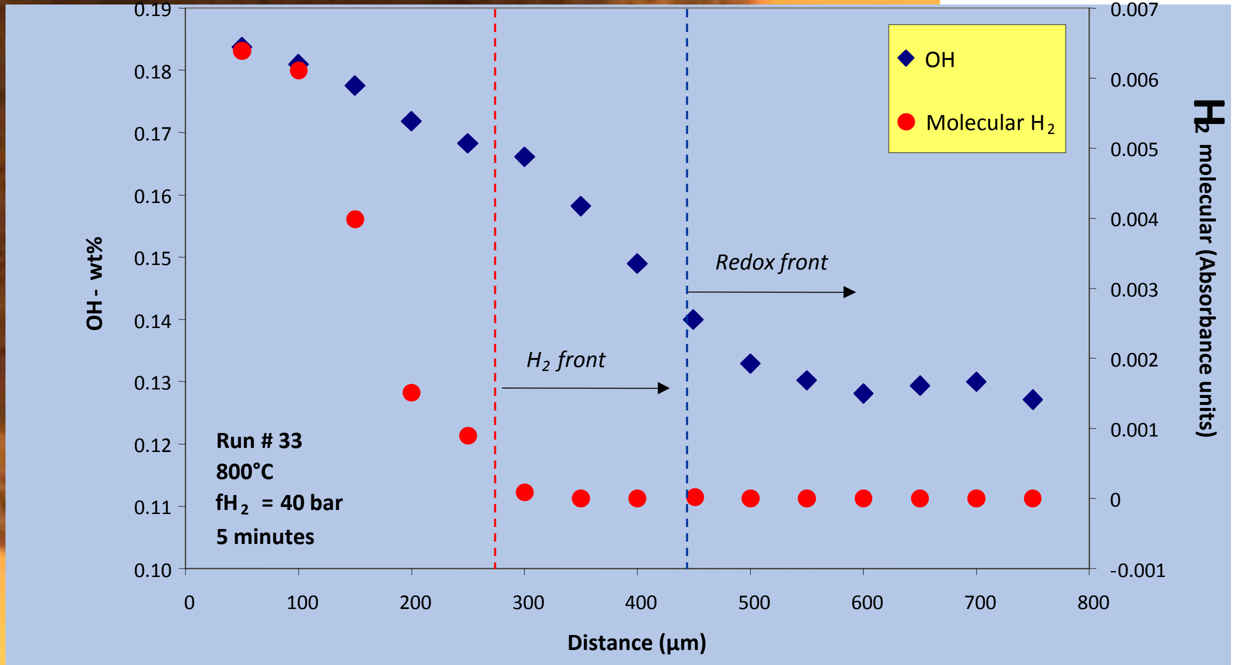
Evidence for the secondary effect of f_{O2} in comparison to f_{H2}



Evidence for incorporation of H in the form H_2 & OH







$$H_2 + Fe_2O_3 => H_2O + 2FeO$$

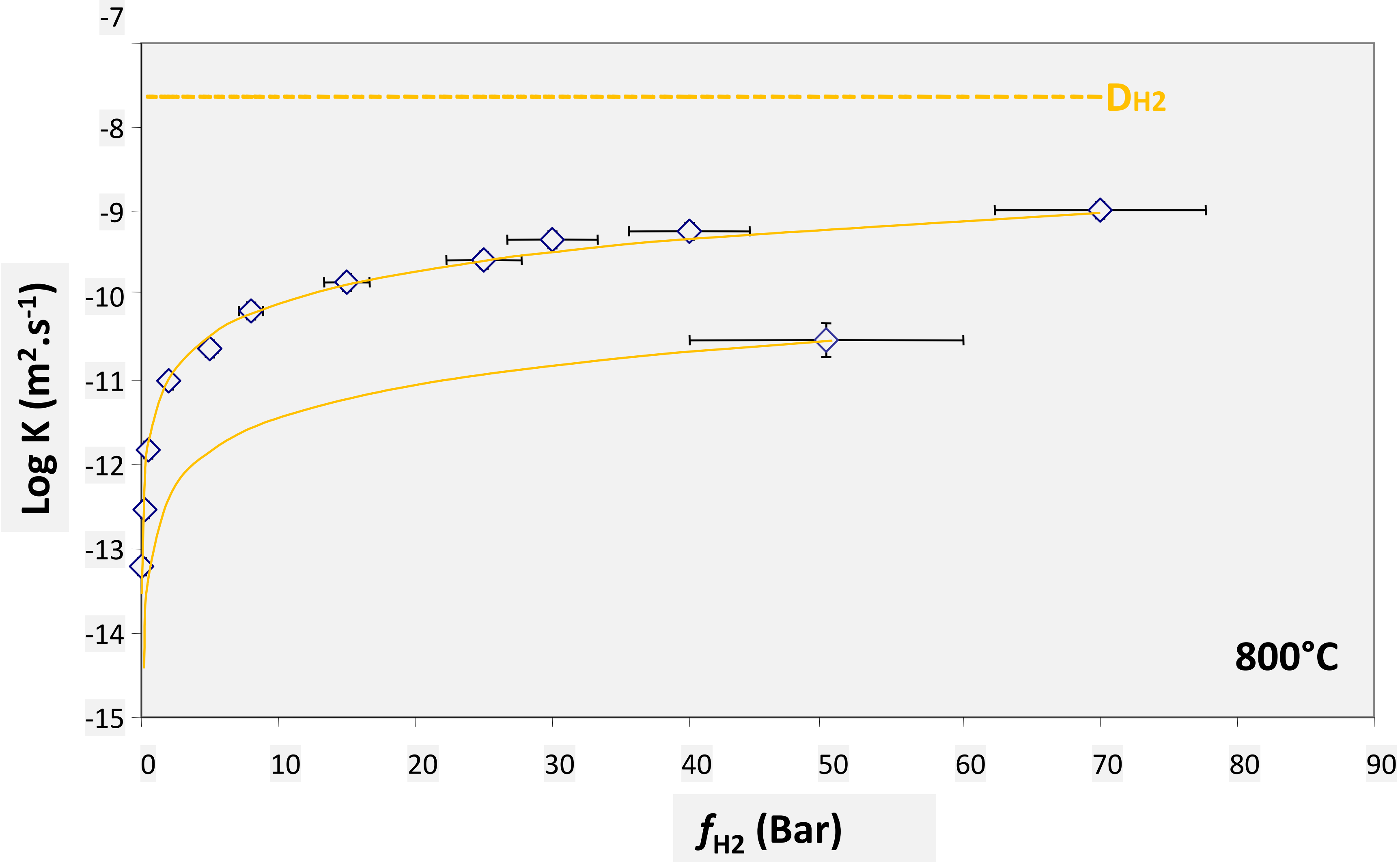
The f_{H2} dependence of the reaction rate: A flux-limited process

$\xi = 2.\,\alpha.\,(D_{H2}\,.t)^{½}$ with $K = 4.\,\alpha^2.\,D$

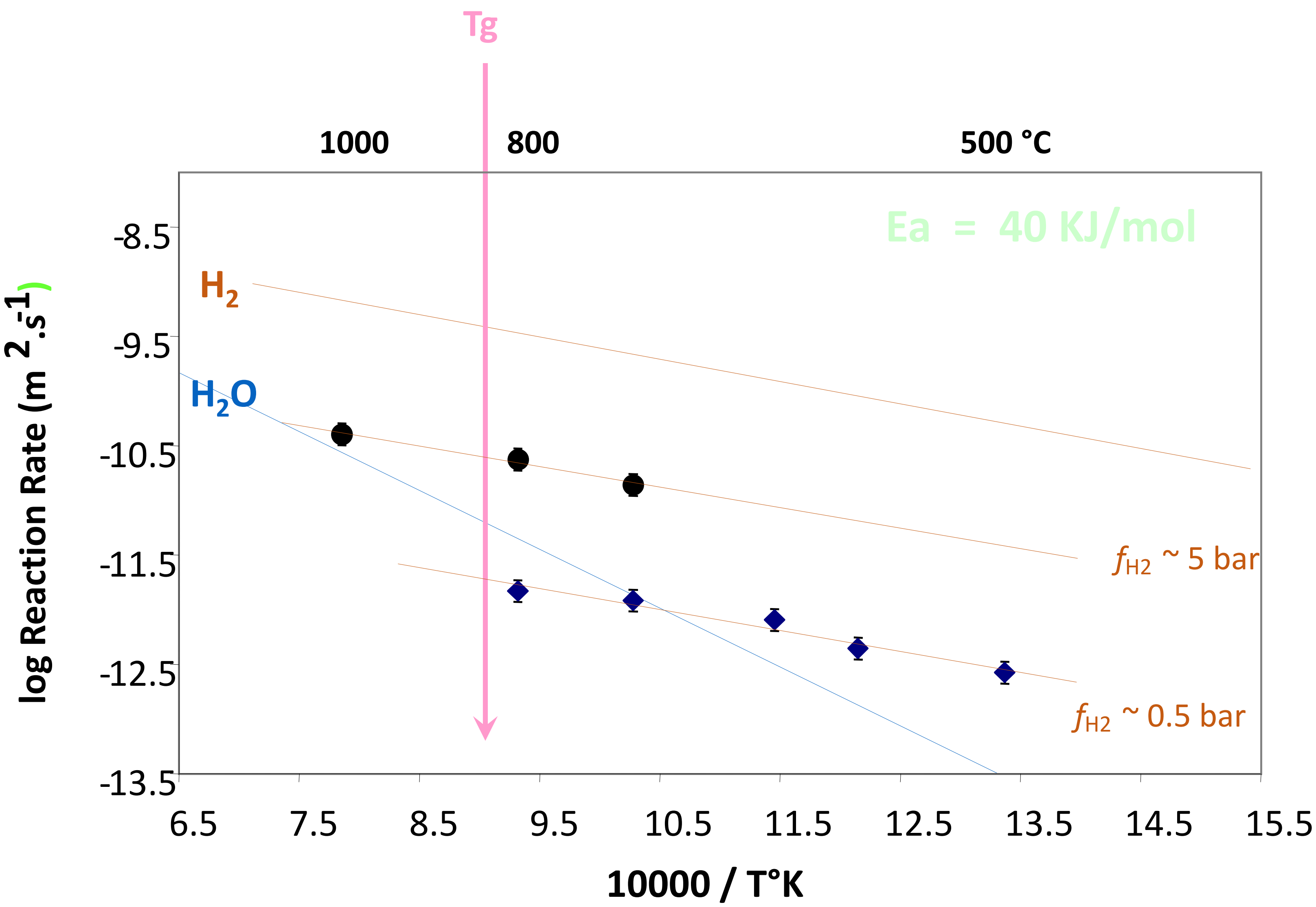
H_2 flux ~ S_{H2} and D_{H2}

$S_{H2} / (\,½\,.C_{OH}\,.\,\rho) = \Pi^{½}\,.\,\alpha\,.\,\exp(\alpha^2)\,.\,\mathrm{erf}\,(\alpha)$

S_{H2} ~ f_{H2}

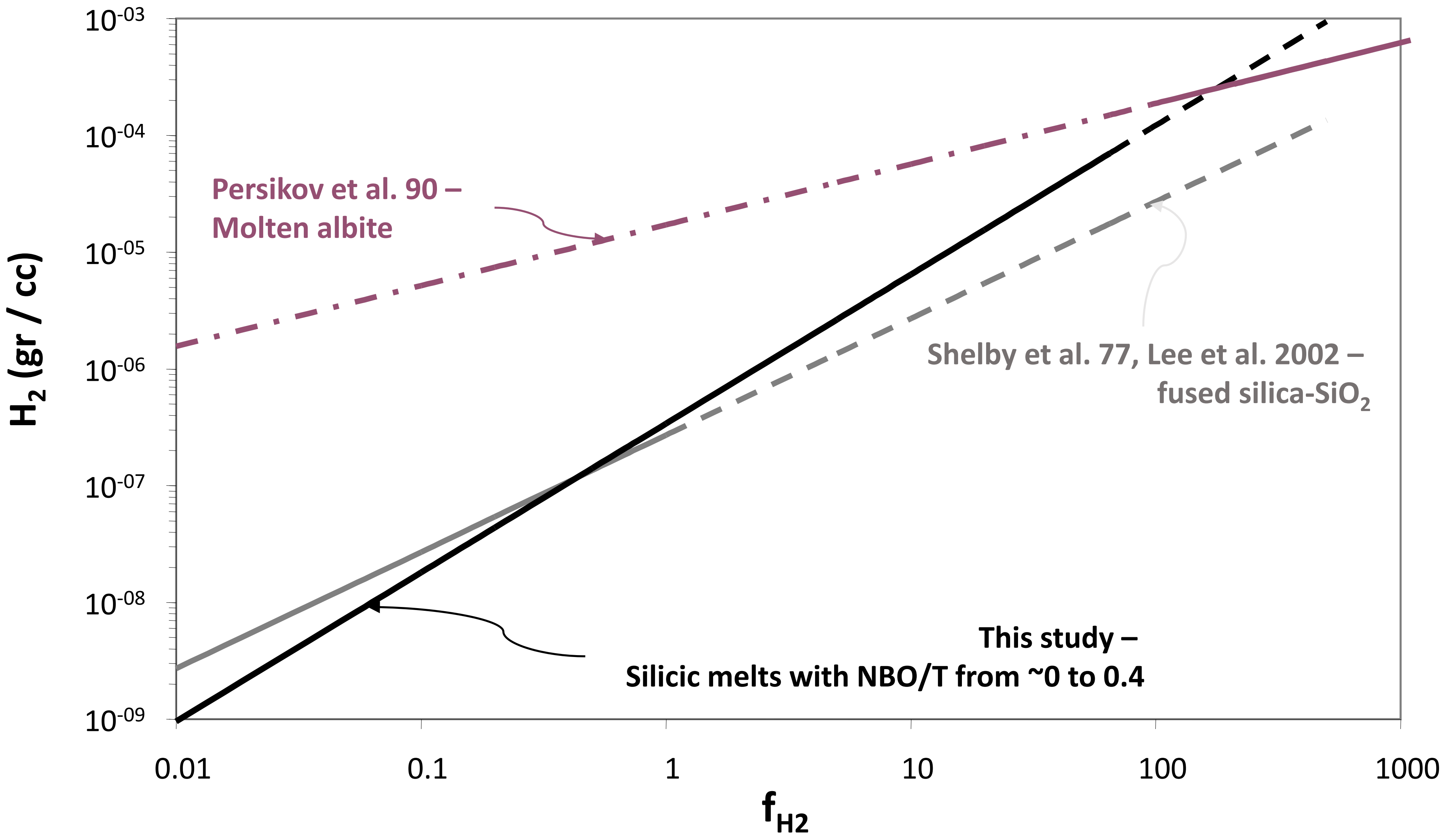


Temperature dependence of the reaction-rate

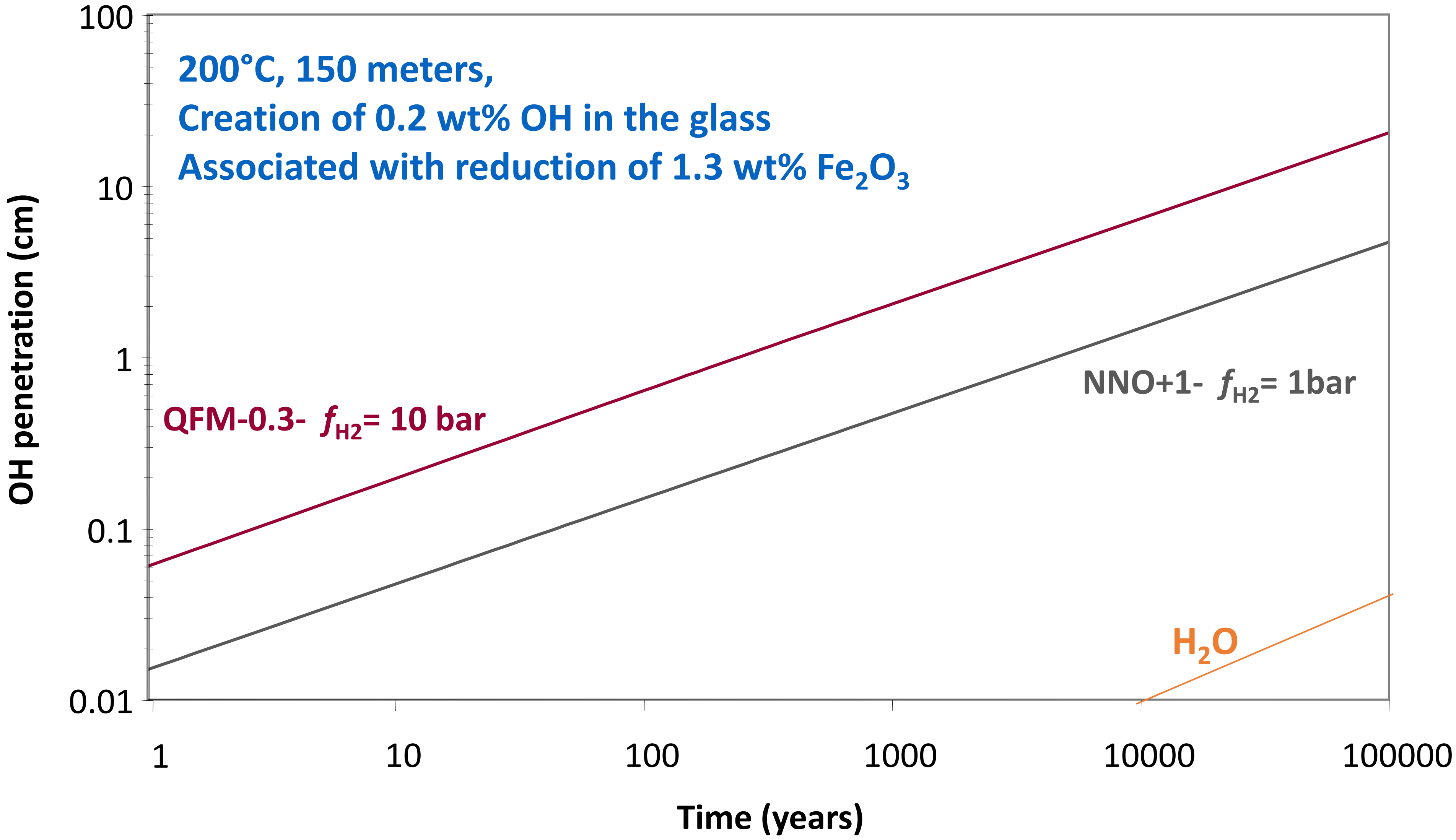


Comparison of model for H_2 solubility in amorphous silicate

H_2 solubility seems independent on the melt structure



Hydration of glasses by incorporation+oxidation of H_2

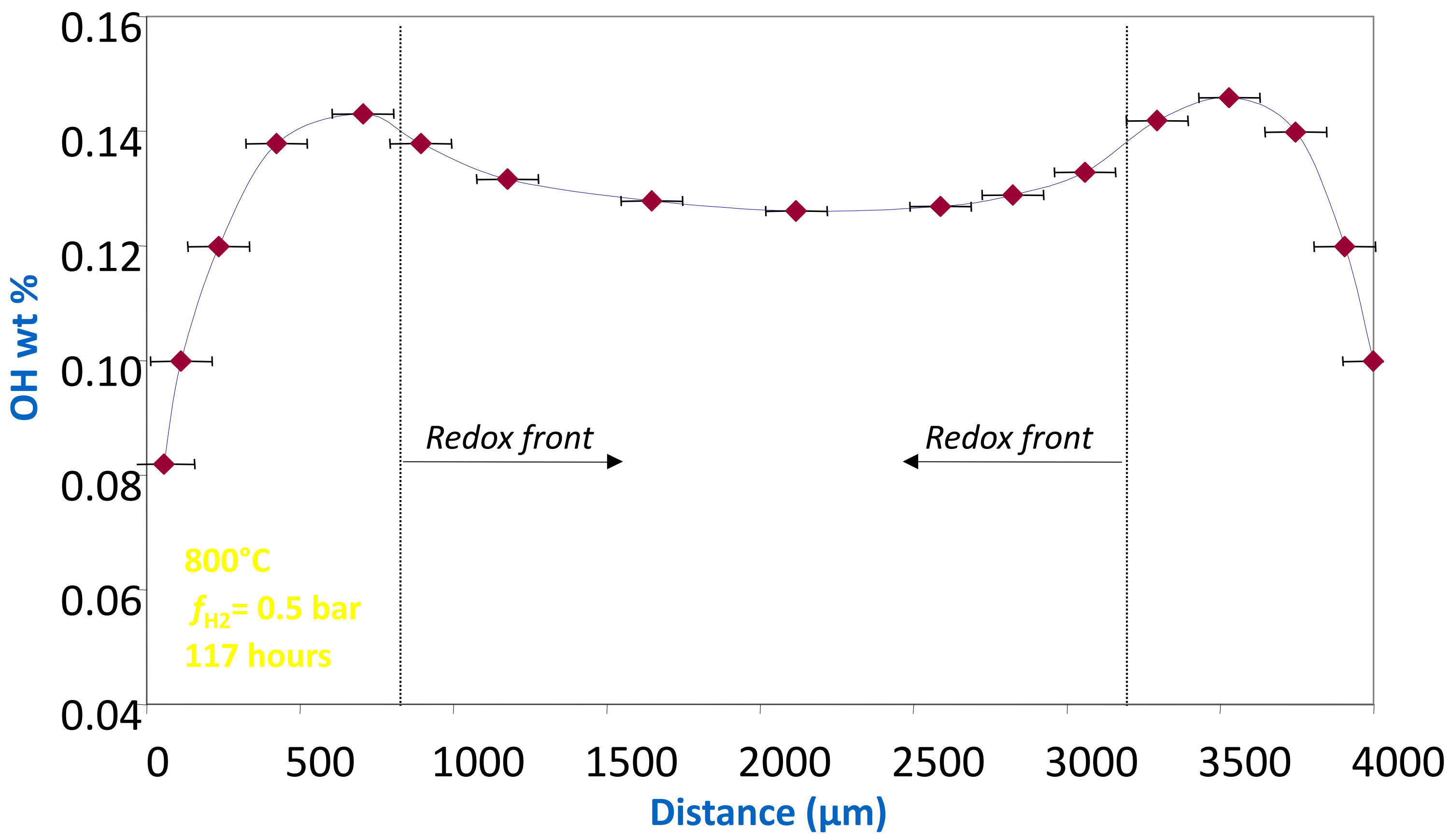


BILAN ET DEMAIN….

- Science de la Terre: diffusion dans le liquide et verre est importante
- Advection + Diffusion
- Diffusion en systemes bi-tri-phases
- La pression pas intrinsequement important, mais
  - Pression = H2O… entre dans la structure, effet sur les D_i
- Redox: oxygene diffuse ou pas? Tracer diffusion de O fiable?
- Hydrogene moleculaire = diffusion, reaction, immobilization… $D>D_{H2O}$

Reversal? Sortie d'H2?

H_2 Incorporation + tranformation into OH + dehydration by H_2O outward migration



Chemical transfer associated with redox exchanges between H_2 and silicate melts: Evidence for Na migration