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DRAGONS ((Device for Reaction Analysis of Gas on Solids))

F. Rouillard

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F. Rouillard. DRAGONS ((Device for Reaction Analysis of Gas on Solids)): A specific device for a better understanding of gas-solid reactions. GRS 2015 - Gordon Research Seminar3 2015, Jul 2015, New London, United States. cea-02489565

HAL Id: cea-02489565

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DRAGONS (**D**evice for **R**eaction ANALYSIS OF **G**AS ON **S**OLIDS)

A SPECIFIC DEVICE FOR A BETTER
UNDERSTANDING OF GAS-SOLID
REACTIONS

GRS 2015 | *Fabien Rouillard*

DPC/SCCME/LECNA

25TH JULY 2015

WHO I AM ?

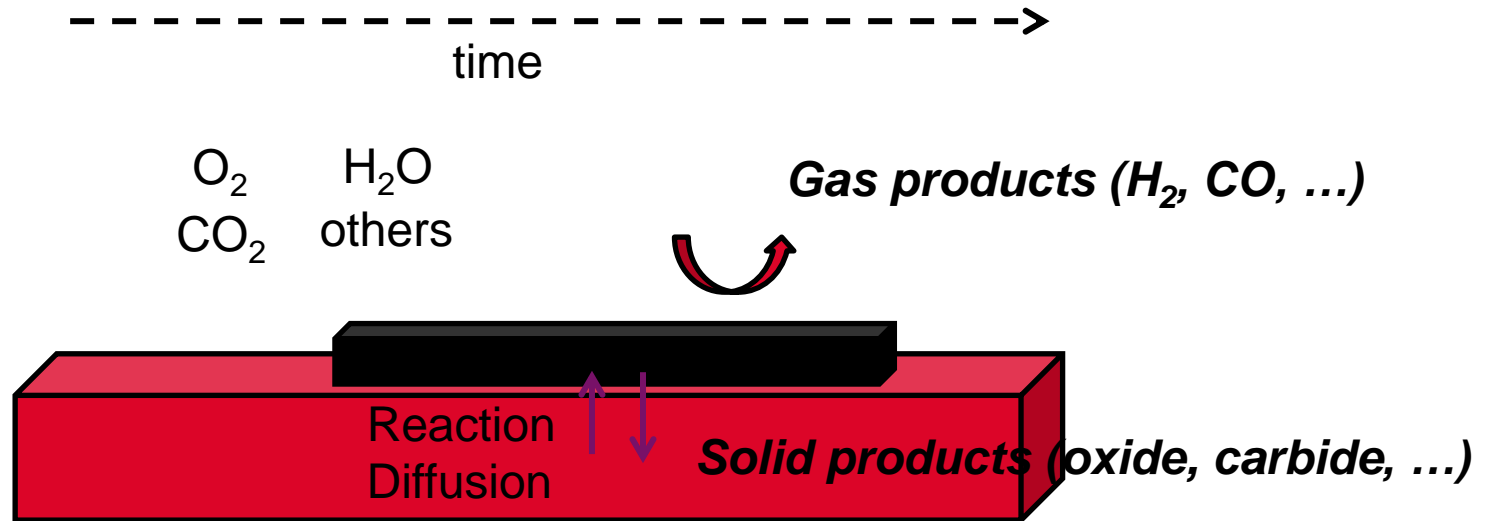
- 2004-2007 : PhD at CEA/Saclay : « Corrosion behaviour of nickel base alloys in impure Helium for Very High Temperature Reactor »

- Since 2008 : Research engineer at CEA/Saclay :
Corrosion studies in
 - gas : water vapor, CO₂

 - Metal liquid : Na (Sodium Fast Reactor)

Interested in the understanding of competition between gas molecules, the selectivity of oxide formation in alloys , the growth mechanism of corrosion layers

GAS SOLID REACTION



Several reaction steps : from molecular dissociation to reaction and diffusion

In most cases, complex alloy with complex atmospheres

Feedbacks have shown that the alloy composition and the atmospheres composition strongly influences the corrosion behaviour from the very first instants of reaction



Development of a facility allowing the detailed study of gas-solid reaction

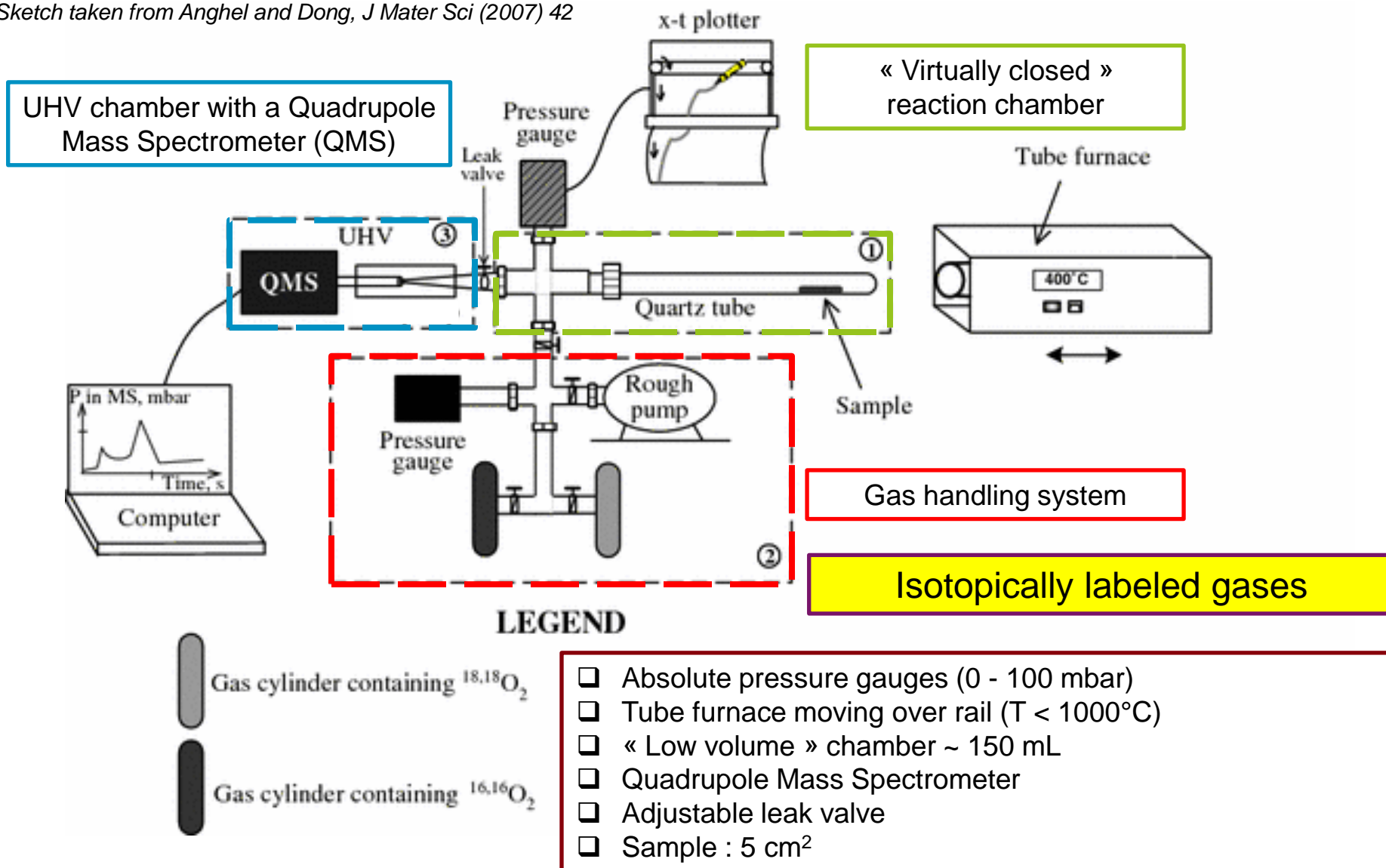
DRAGONS

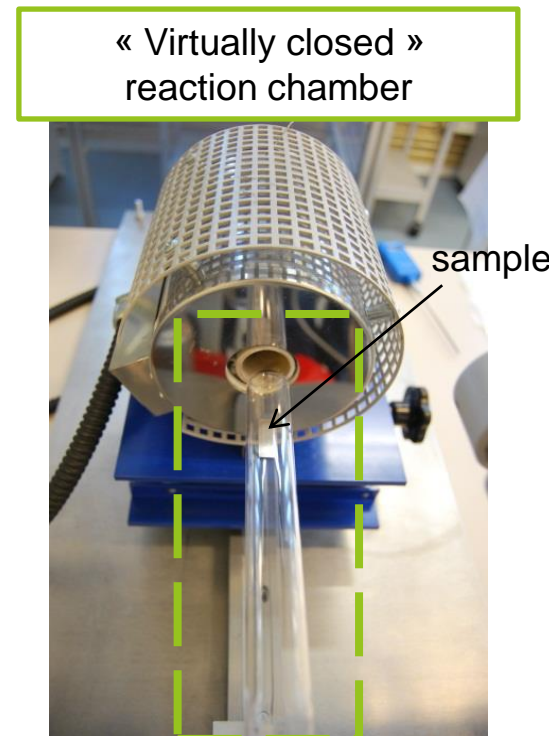
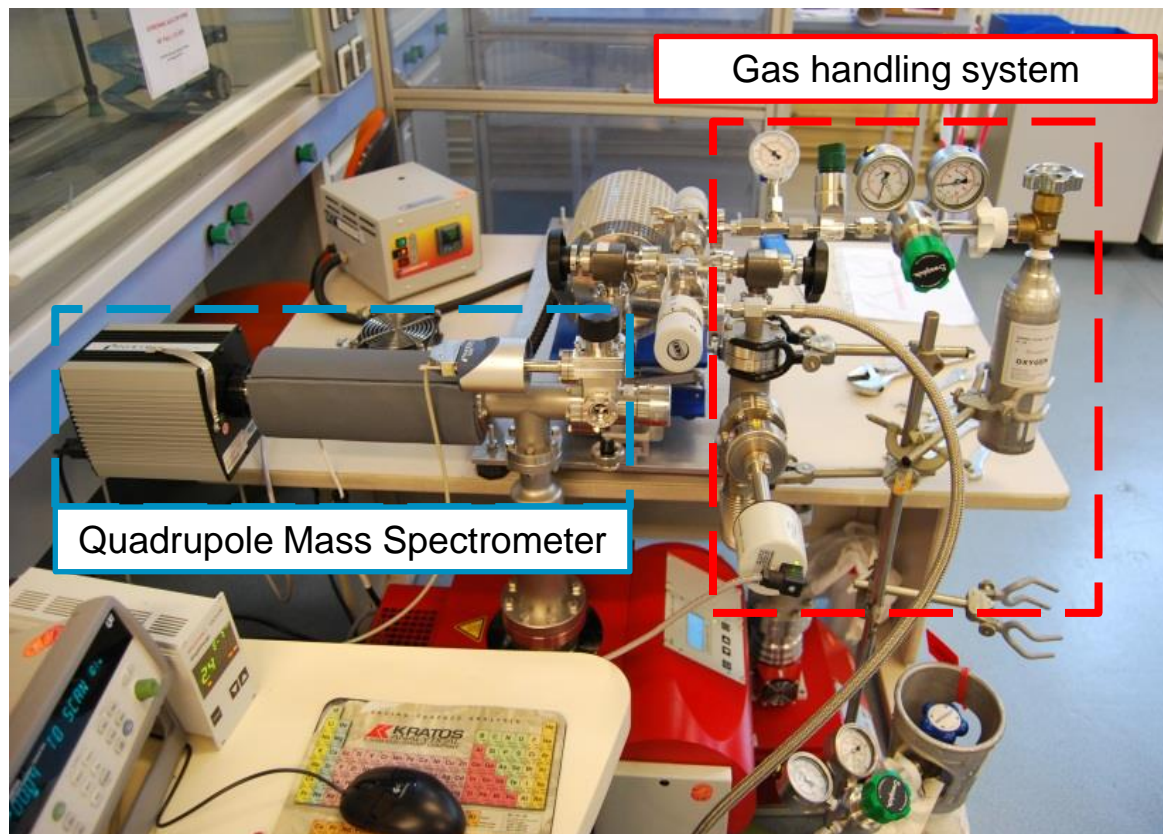
(DEVICE FOR REACTION ANALYSIS
OF GAS ON SOLID)

Development from articles by
**G. Hultquist, Akermark, Wallinder, Anghel,
Dong and colleagues**
[Royal Institute of Technology, Stockholm]
1993 – 2009
Winter and Boreskov in earlier studies in the
50's and 60's

DESCRIPTION OF DRAGONS

Sketch taken from Anghel and Dong, *J Mater Sci* (2007) 42





- ❑ Measurement of the **dissociative rate** of gas molecules
- ❑ Study of **gas transport parameters** in oxide scales (diffusivity, permeability)
- ❑ Study of **reaction mechanism** between mixed gas phase and solid

DISSOCIATION OF GAS MOLECULES ON SOLID SURFACE

G. Hultquist et al.

Winter et al.

Boreskov et al.

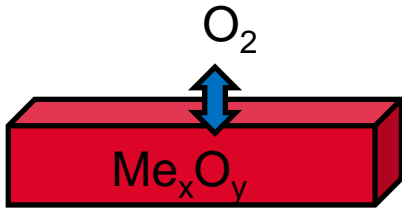
HOW DO WE DO ? EXAMPLE OF O₂

- Sample with a binary labeled gas mixture $^{16,16}\text{O}_2$ - $^{18,18}\text{O}_2$
- Measurement of the formation rate of $^{18,16}\text{O}_2$

A SPECIFIC DEVICE BASED ON ISOTOPIC EXCHANGE



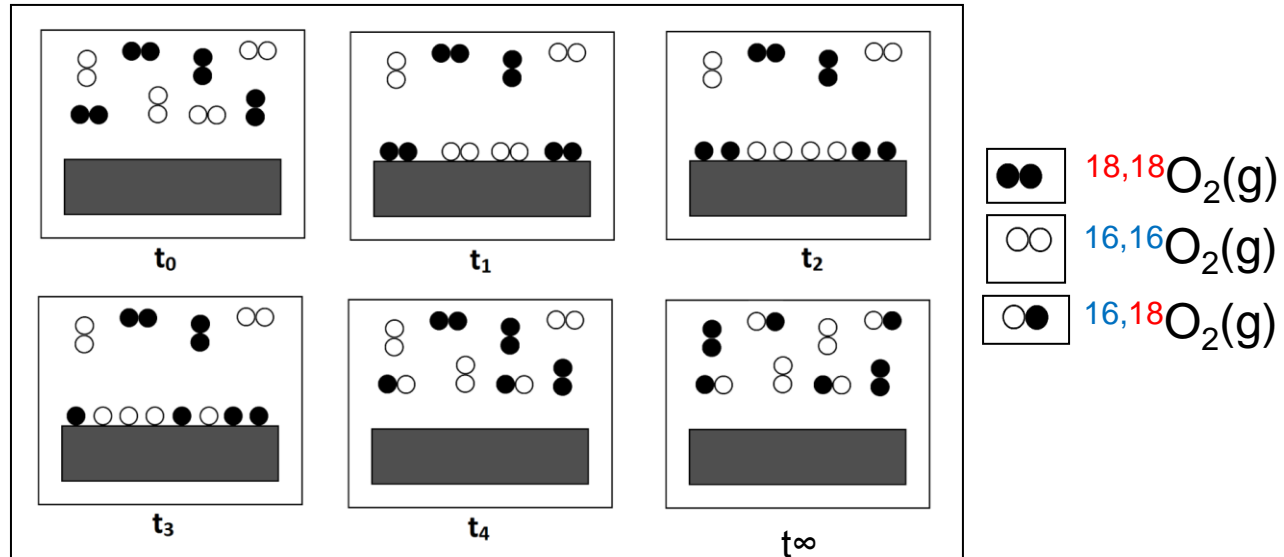
O exchange between O_2 molecules on solid surface



Exchange between O_2 and [O] from the oxide surface

$^{18,16}\text{O}_2$ is mainly formed by these two processes

Binary mixture $^{18,18}\text{O}_2(\text{g}) + ^{16,16}\text{O}_2(\text{g})$



Statistical equilibrated gas composition

At $t = t^\infty$:

$$C_\infty^{16,18} = P^{16,18} \times \frac{n}{V}$$

$C_\infty^{16,18}$: $^{16,18}\text{O}_2(\text{g})$ concentration at equilibrium (mol/m^3)
 $P^{16,18}$: Probability to form $^{16,18}\text{O}_2(\text{g})$
 n : Molar quantity of $\text{O}_2(\text{g})$ (mol)
 V : Reactor volume (m^3)

$^{16,18}\text{O}_2$ concentration $C^{16,18}(t)$ as function of time :

$$C^{16,18}(t) = C_{\infty}^{16,18} + (C_0^{16,18} - C_{\infty}^{16,18}) \exp\left(-\frac{P^{16,18}bt}{C_{\infty}^{16,18}}\right)$$

Probability to form $^{16,18}\text{O}_2(\text{g})$

$^{16,18}\text{O}_2(\text{g})$ concentration at equilibrium

Initial $^{16,18}\text{O}_2(\text{g})$ concentration

b : Unknown ($\text{mol}/\text{cm}^3/\text{h}$)

Involves adsorption, dissociation, re-formation and desorption of O_2

In order to take into account the possible pressure decrease in the reactor due to oxidation :

Use of fractions $f = P/P^{\text{total}}$

[assumption: $v(\text{Adsorption}) = k \cdot P$]

$$f^{16,18}(t) = f_{\infty}^{16,18} + (f_0^{16,18} - f_{\infty}^{16,18}) \exp\left(\frac{P^{16,18} B t}{f_{\infty}^{16,18}}\right)$$

$B \text{ (h}^{-1}\text{)}$
=
Fitting parameter

$$\frac{b}{C_0^{\text{tot}}} = B$$



$b \text{ (mol/cm}^3\text{/h)}$

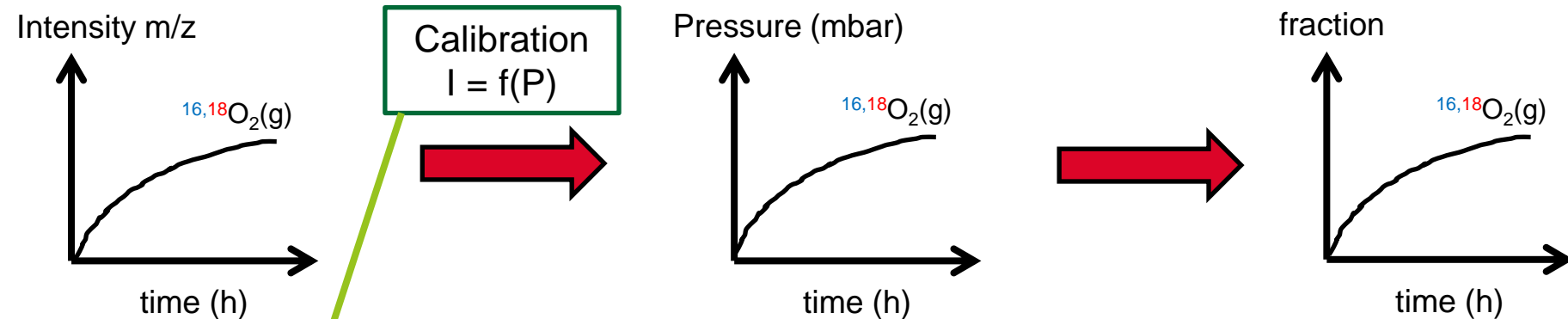


$$v_d = \frac{2b \cdot V}{S}$$

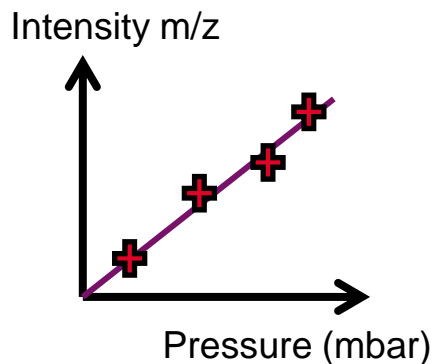
Sample surface (cm²)

Dissociative rate of O₂
(μmole O/cm²/h)

EXPERIMENTALLY ?

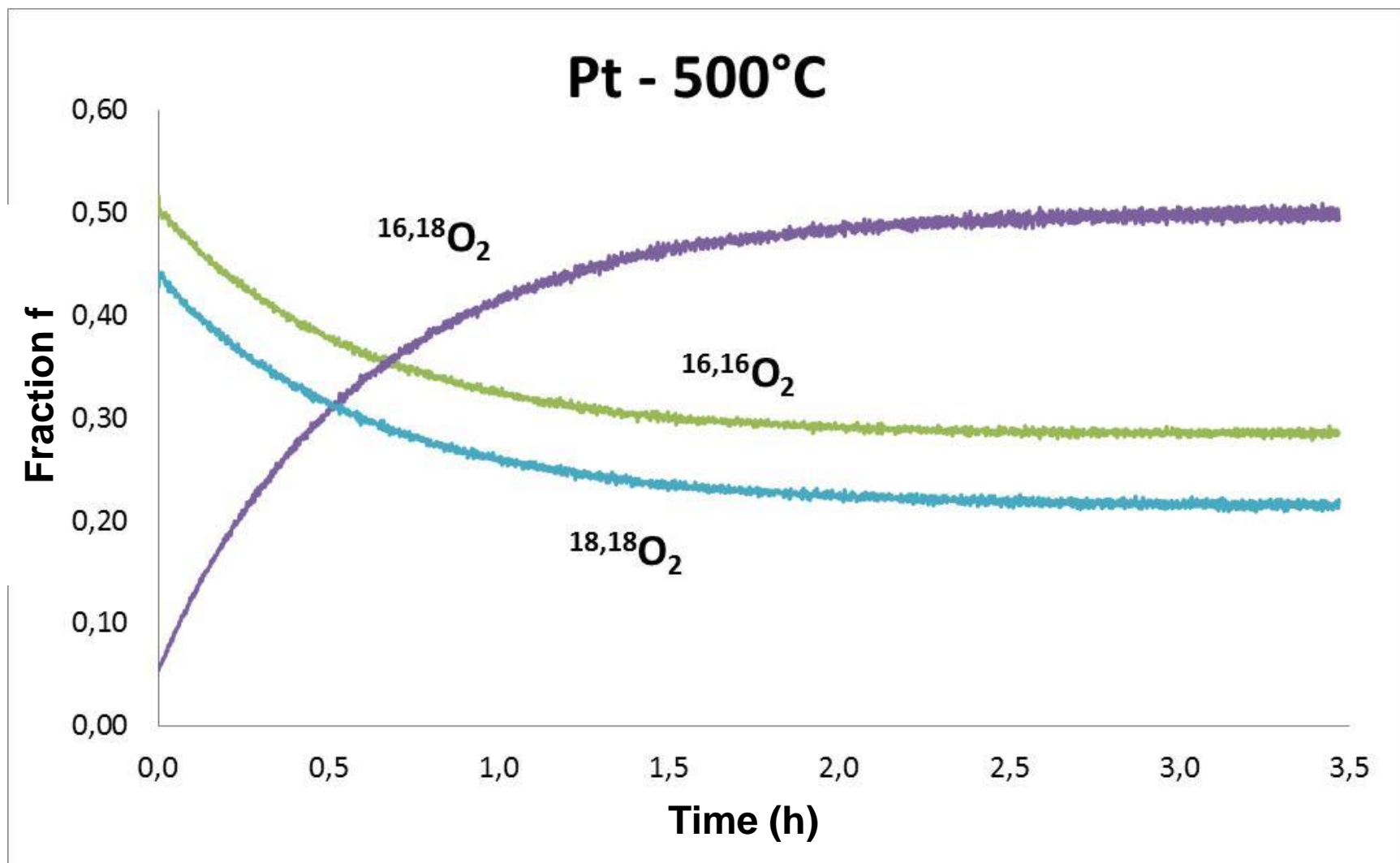


$I=f(P)$ calibration



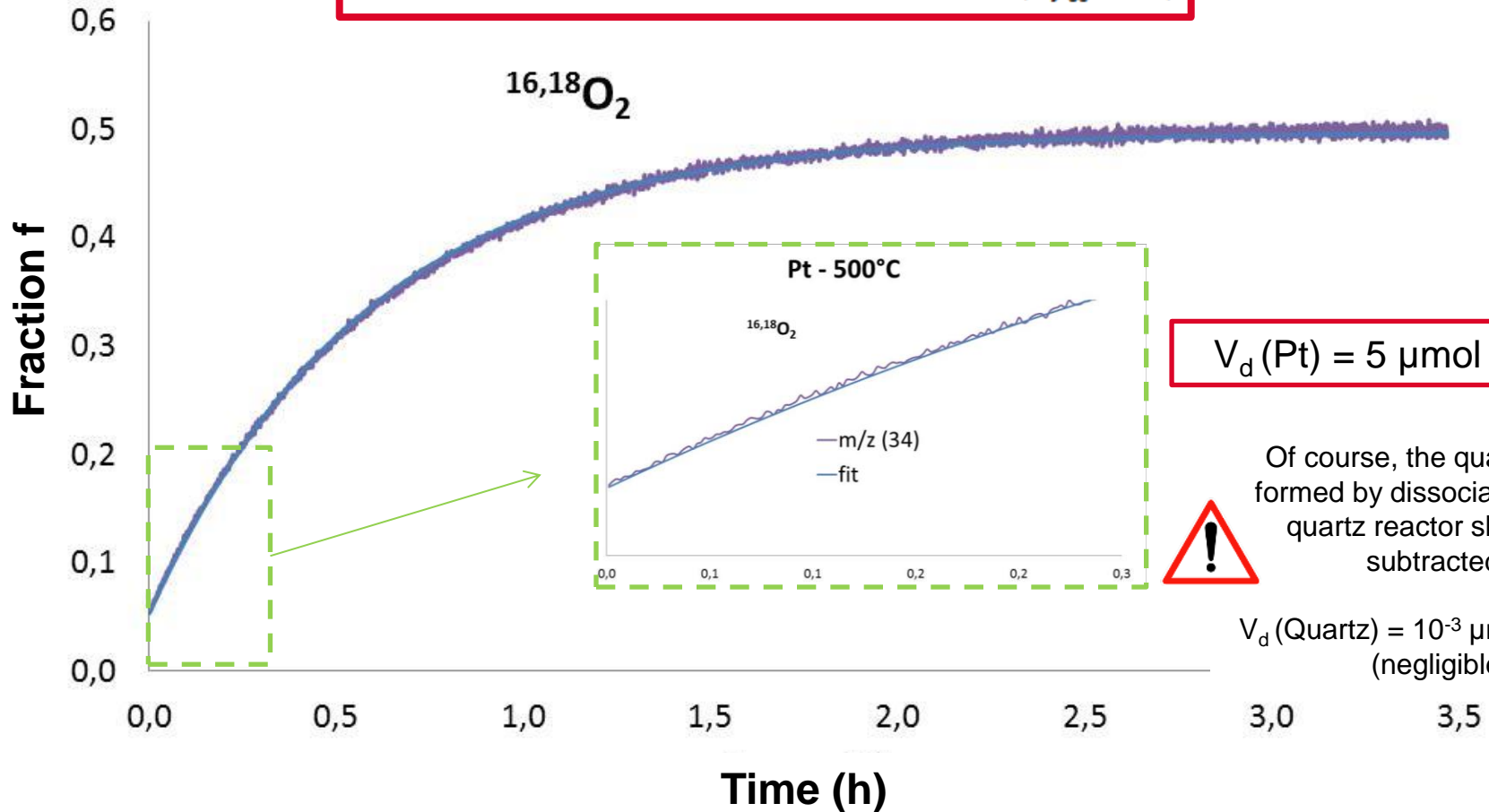
Injection of several $^{x,x}\text{O}_2$ gas pressures into the reactor and measurement of respective I on the QMS :

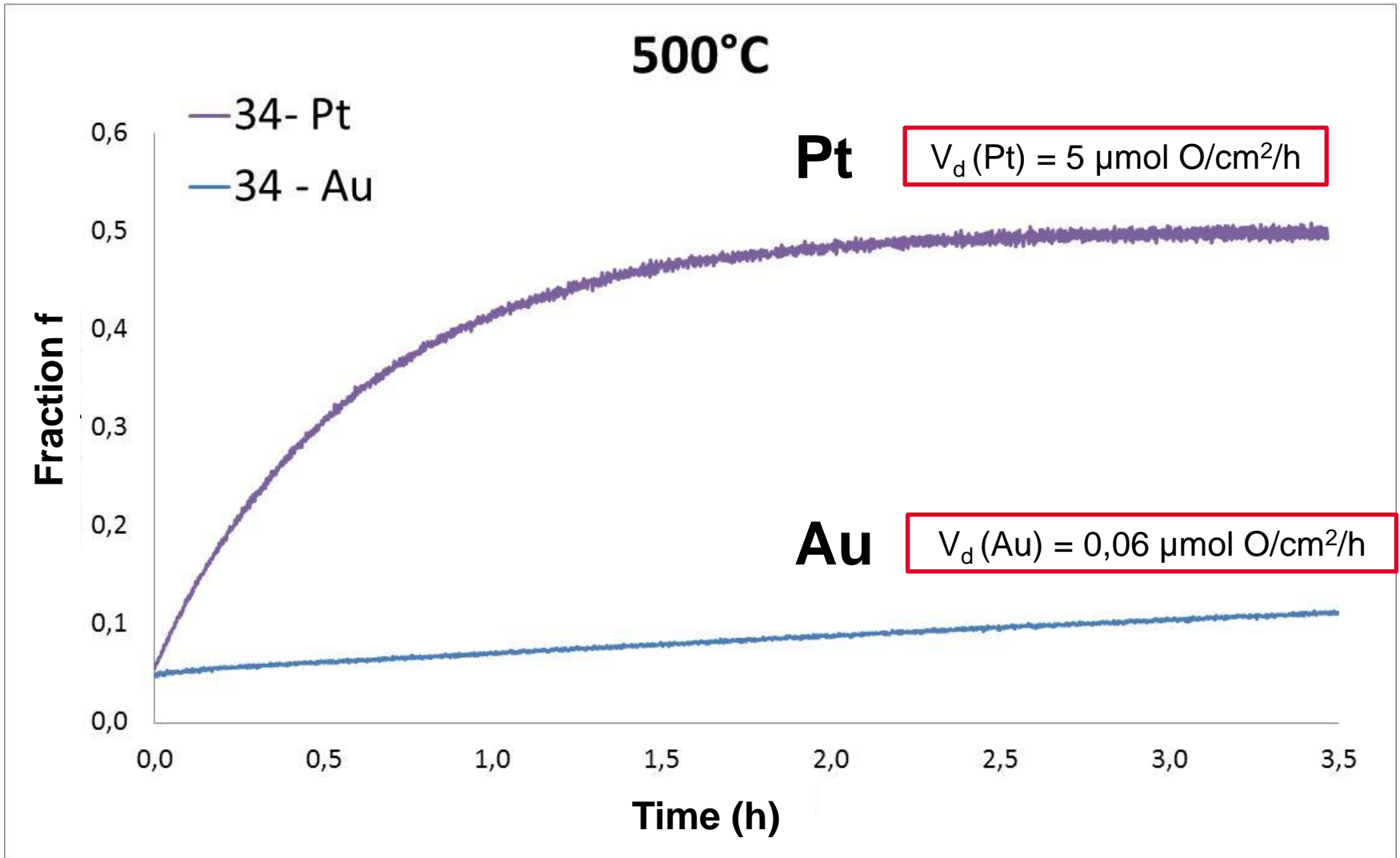
- On « pure » $^{16,16}\text{O}_2$
- On « pure » $^{18,18}\text{O}_2$

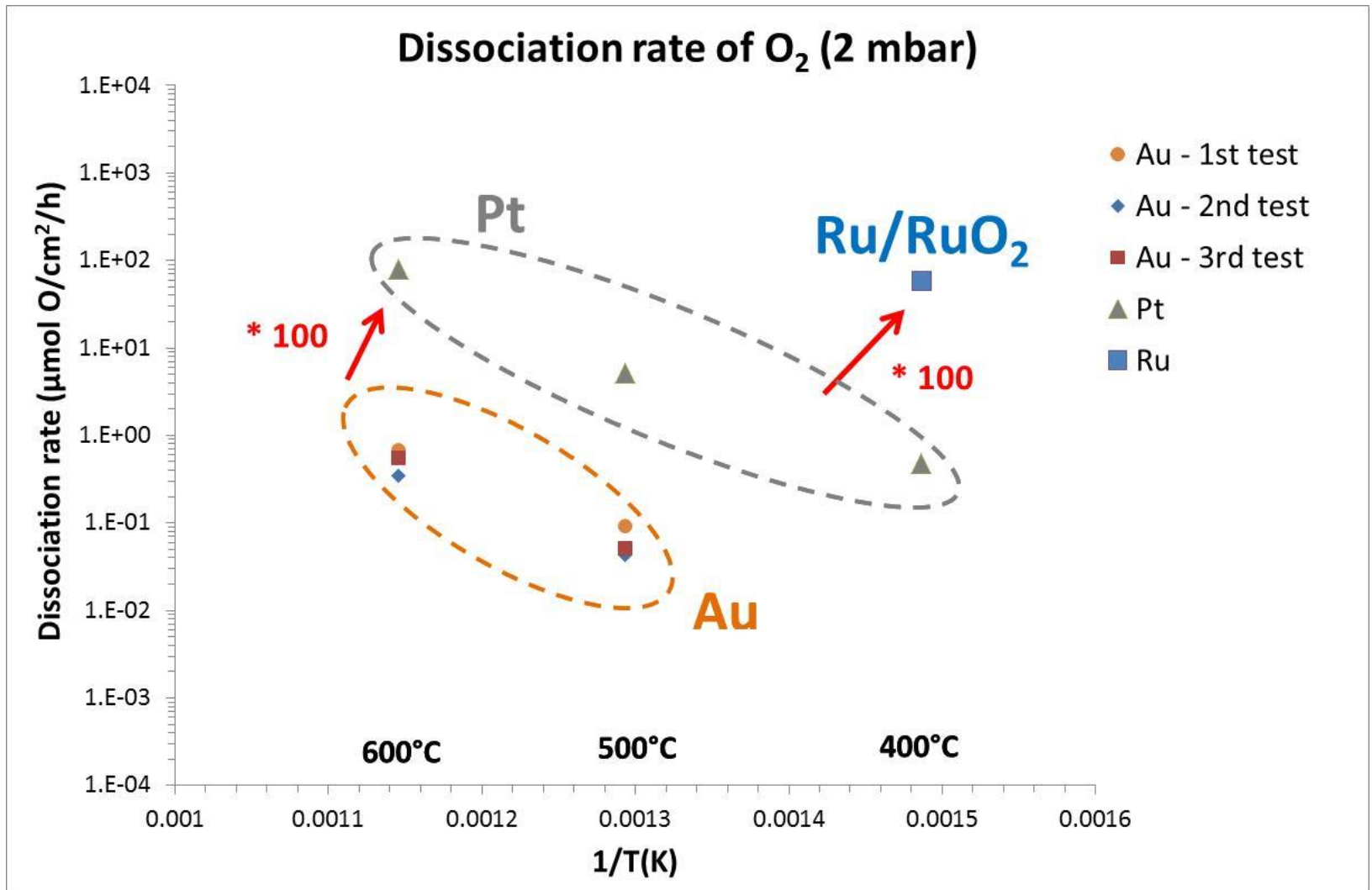


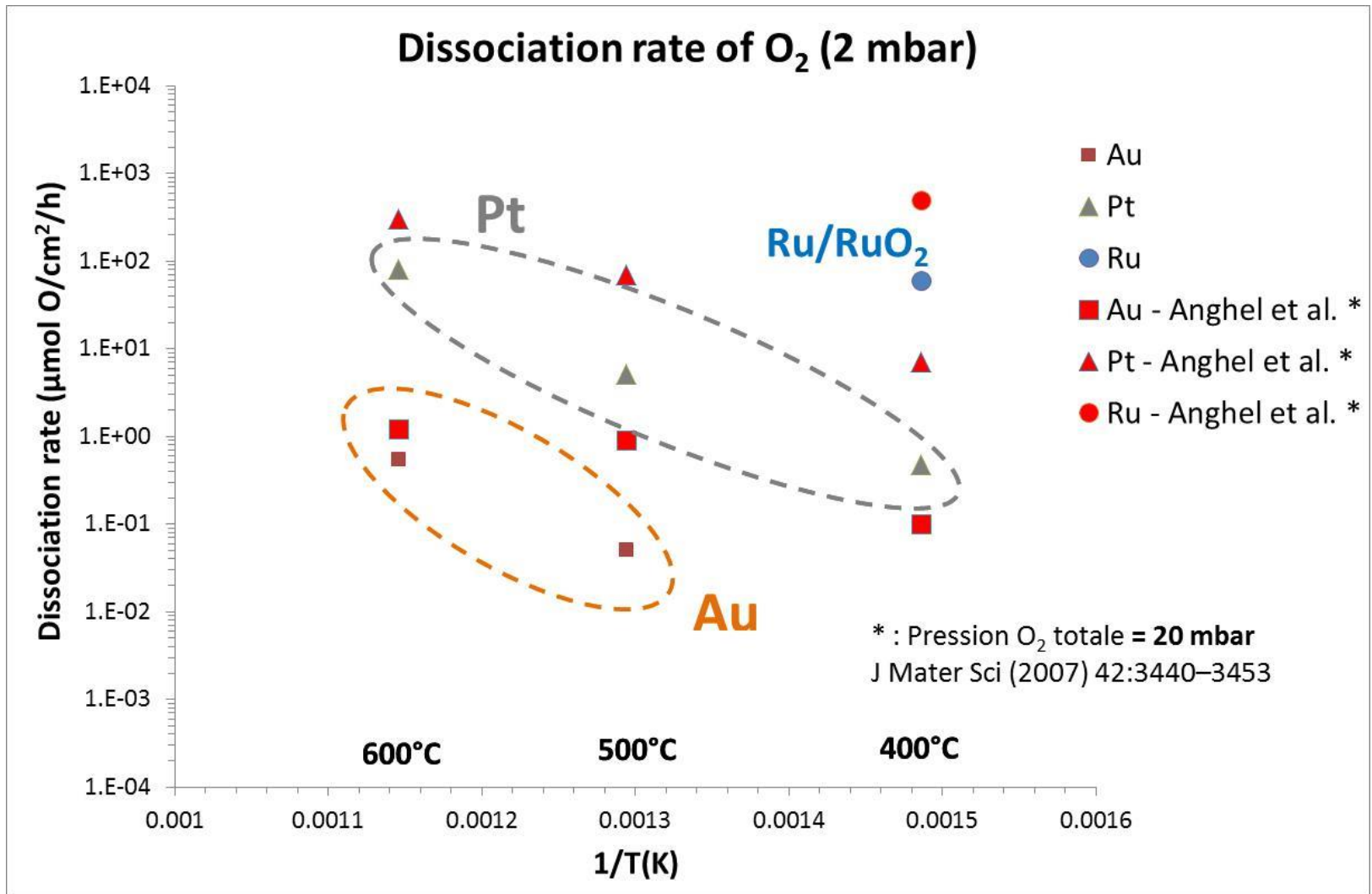
Fitting parameter

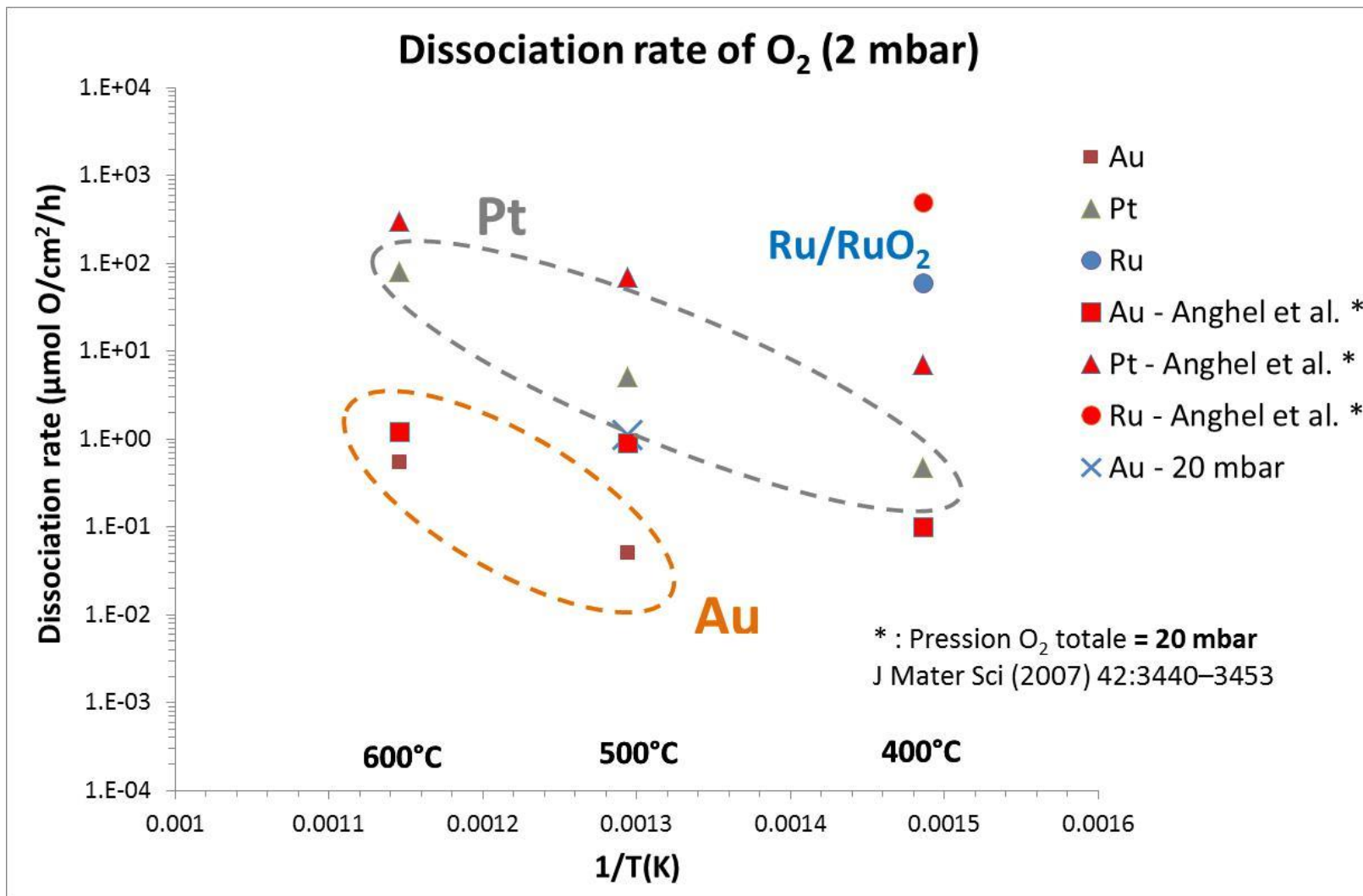
$$f^{16,18}(t) = f_{\infty}^{16,18} + (f_0^{16,18} - f_{\infty}^{16,18}) \exp\left(\frac{P^{16,18} B t}{f_{\infty}^{16,18}}\right)$$











The dissociation rate increases with P

DISSOCIATION : A MINOR EVENT

Gas Kinetics Theory

$$Z = P(2\pi kTM)^{-1/2} \quad (\text{collision/m}^2/\text{s})$$

Numerical application :

$$P = 1 \text{ mbar}$$

$$k = 1,38 \cdot 10^{-23} \text{ J/K}$$

$$M(\text{O}_2) = 5,3 \cdot 10^{-26} \text{ kg/molecule}$$

$$T = 823 \text{ K}$$

$$Z = 1.6 \cdot 10^{24} \text{ collision/m}^2/\text{s}$$

To compare to

$$V_d (823 \text{ K, Pt}) = 8.4 \cdot 10^{18} \text{ atom O/m}^2/\text{s}$$

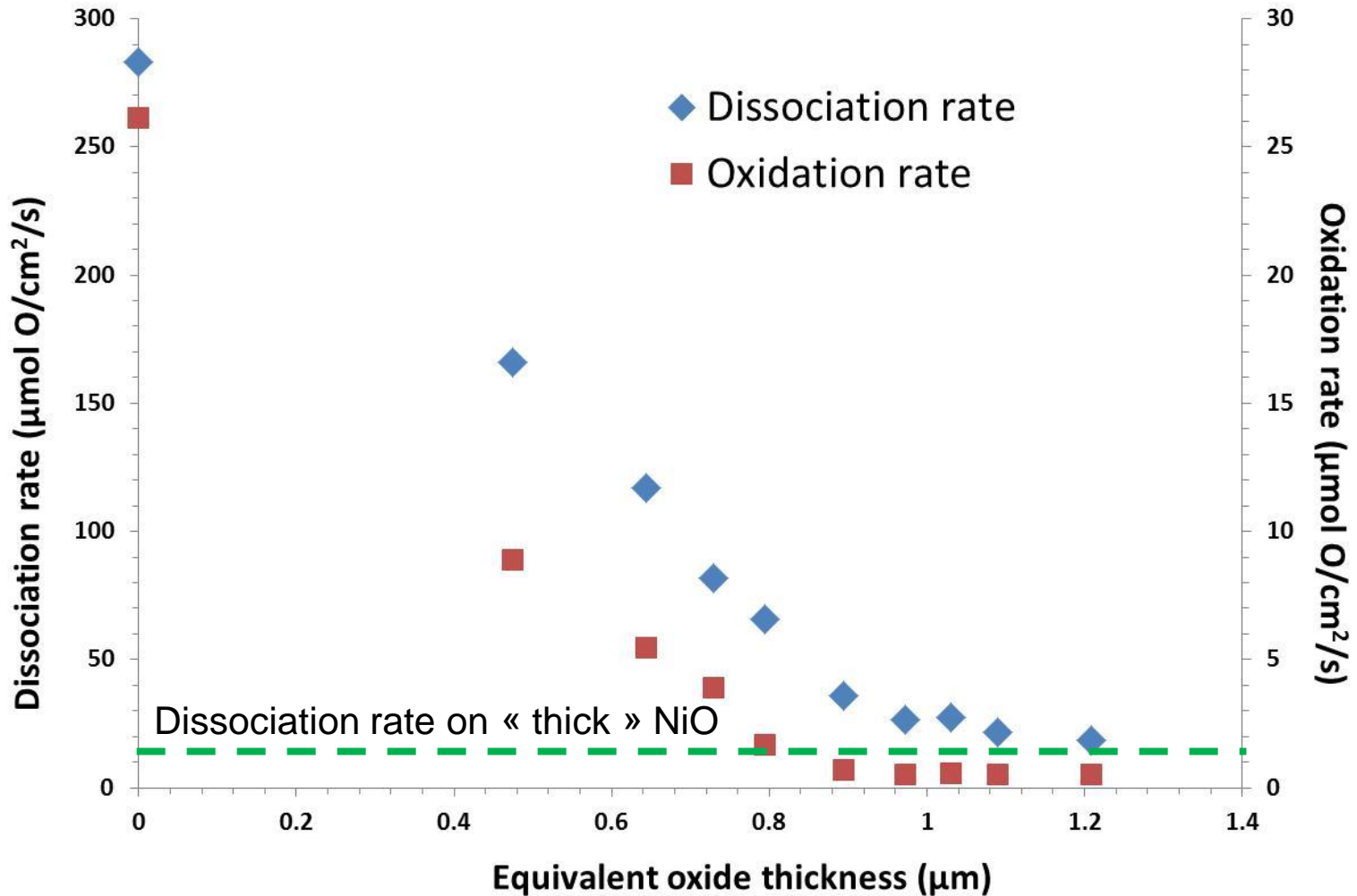
Dissociation probability on Pt $\sim 10^{-5}$

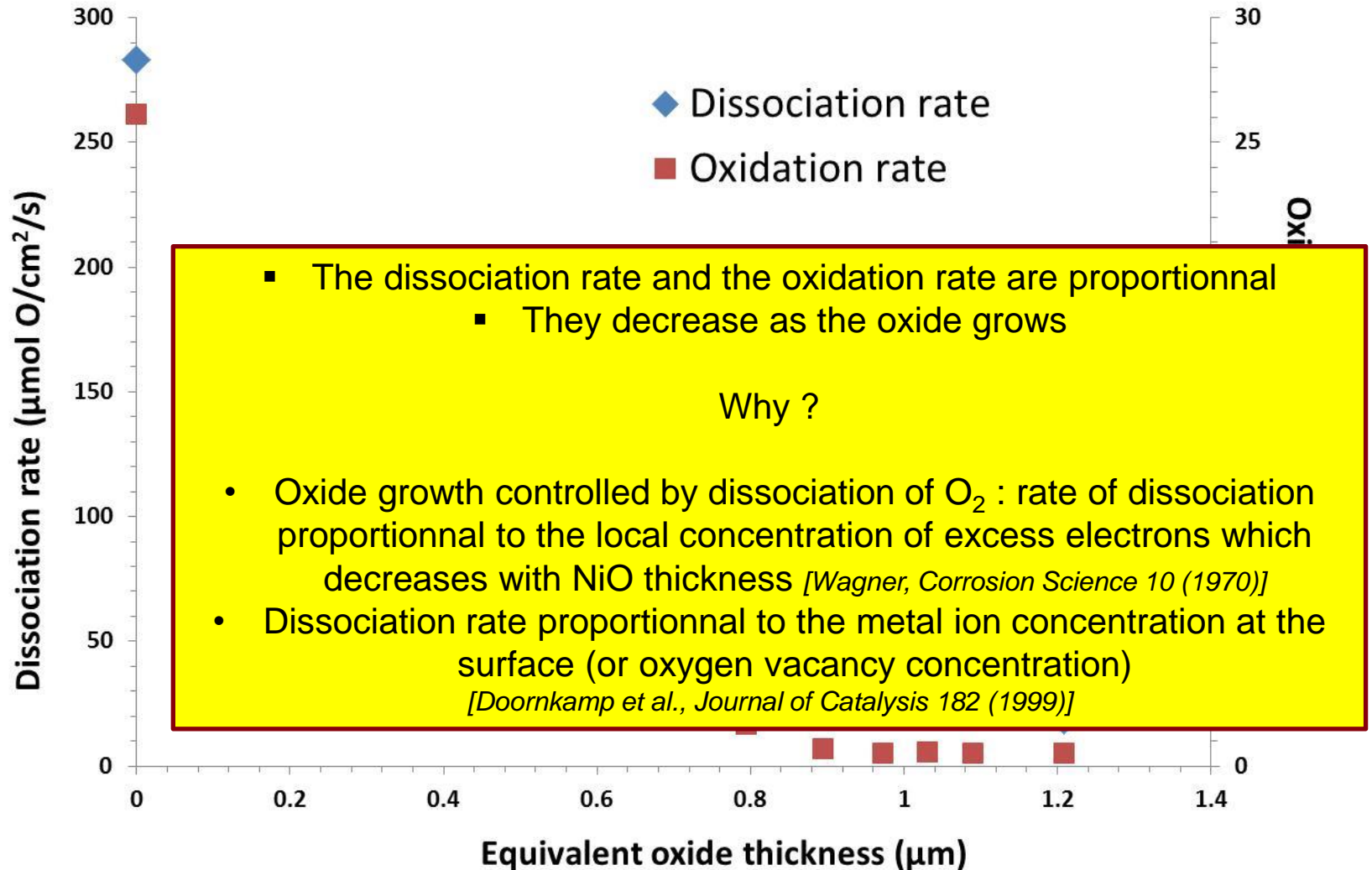


« Active » sites on the surface
(defects, dislocations, high order vacancies ...)

EFFECT OF OXIDE GROWTH ON DISSOCIATION RATE

Oxidation of Ni in binary $^{16,16}\text{O}_2 + ^{18,18}\text{O}_2$ (5 mbar) at 700°C

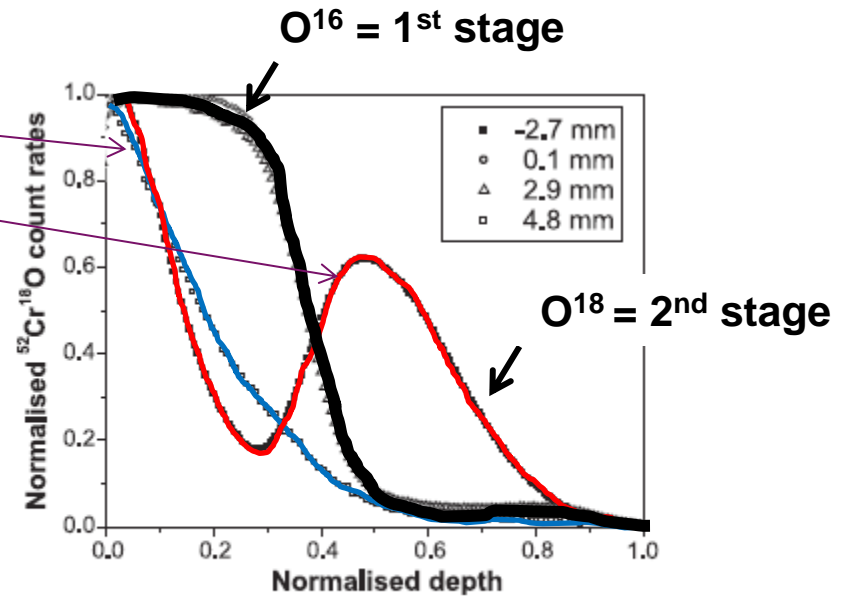
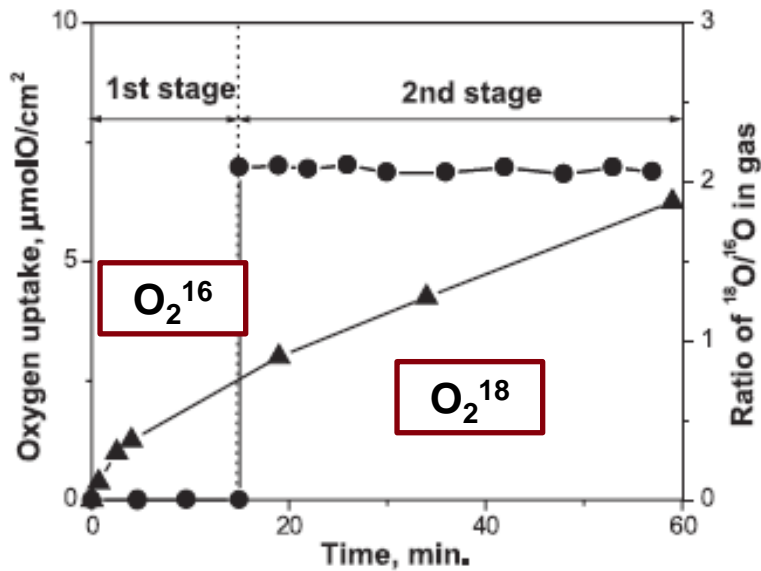
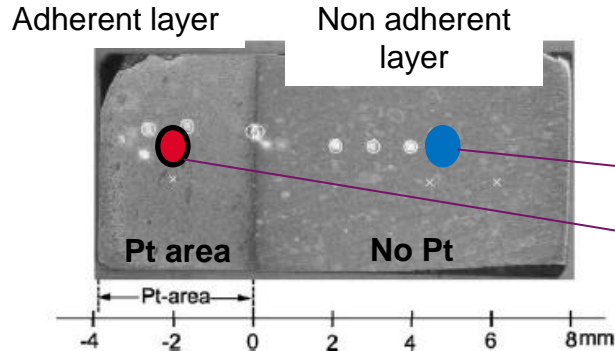




« Engineering » the alloy composition (with minor elements) and the gas composition as a function of their reactivity from dissociation point of view could help producing more corrosion resistant alloy

EFFECT OF « OXYGEN DISSOCIATION ELEMENT » ON OUTWARDS GROWING OXIDE ?

Cr and Cr + Pt under O₂ (800°C) [Hultquist et al. Corrosion Science 45 (2003)]



Improvement of the *oxide adherence* by increasing the dissociation rate of the surface

Increase inwards O flux = no formation of voids at the Oxide/Metal interface

« SELF REPAIRING » OXIDE

Hultquist et al. Oxidation of Metals 56 (2001)

← Increased metal-ion transport due to Hydrogen

→ Increased oxygen-ion transport due to « ODE »

Degree of protection

Degree of protection

Oxide growth at the O/M and G/O interface

Poor scale adherence

Crack formation

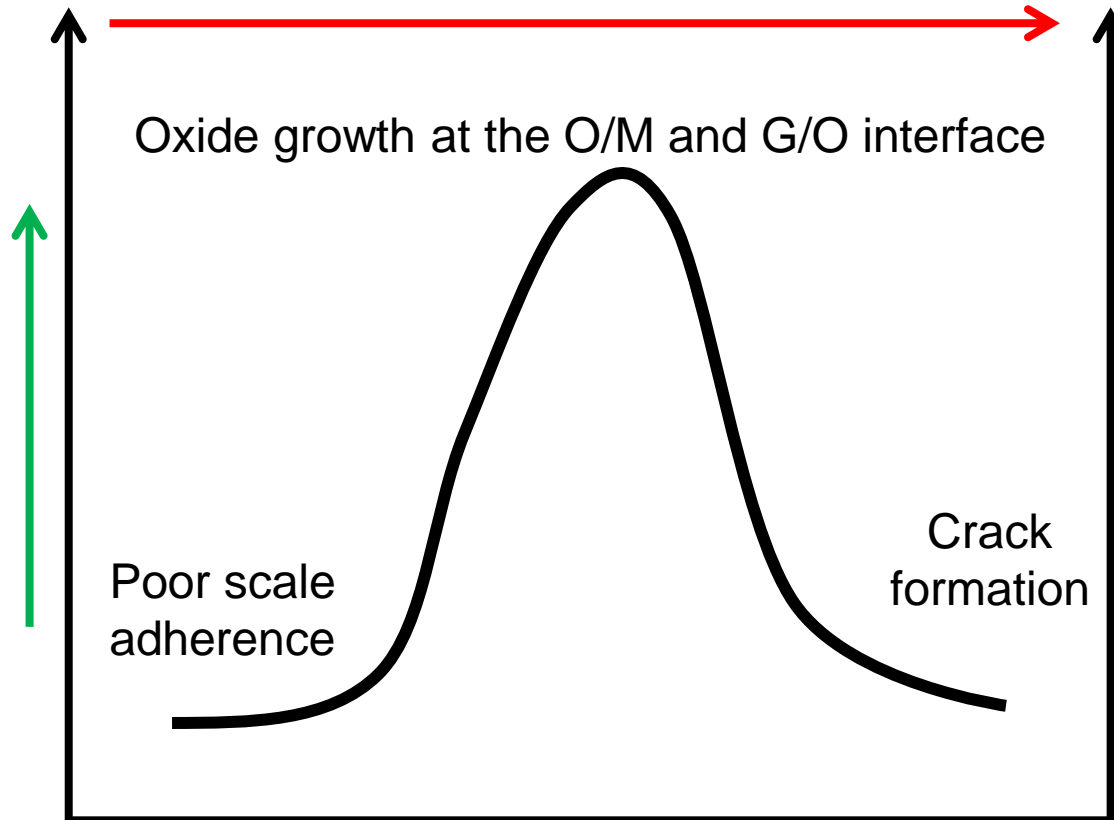
Ex: Cr

Exclusive metal-ion transport

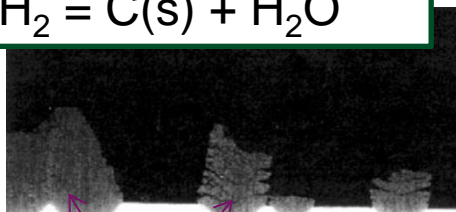
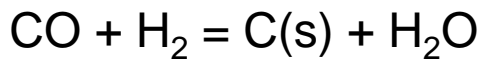
Balanced transport

Exclusive oxygen-ion transport

Ex: Zr



DISSOCIATION SELECTIVITY : EXAMPLE OF METAL DUSTING



AISI 410
300 μm

Coke formation

Stainless steel AISI 410 after 100 h under
73.2 % H₂ – 24.4 % CO – 2.4 % H₂O at 560°C

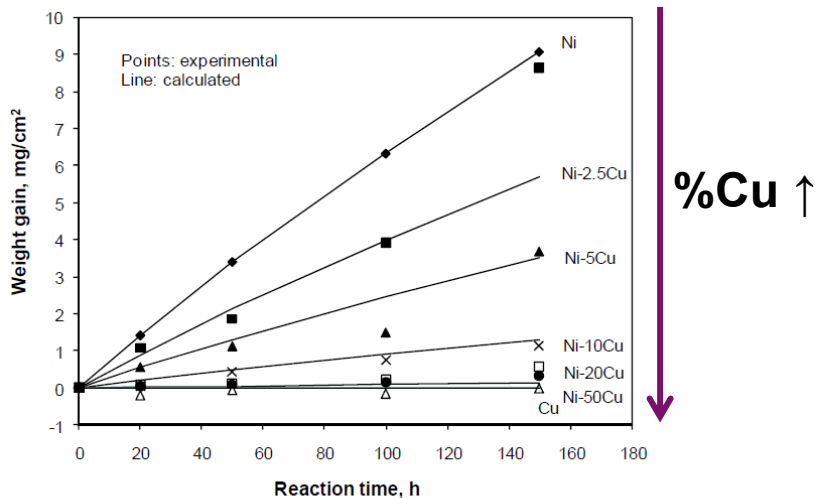
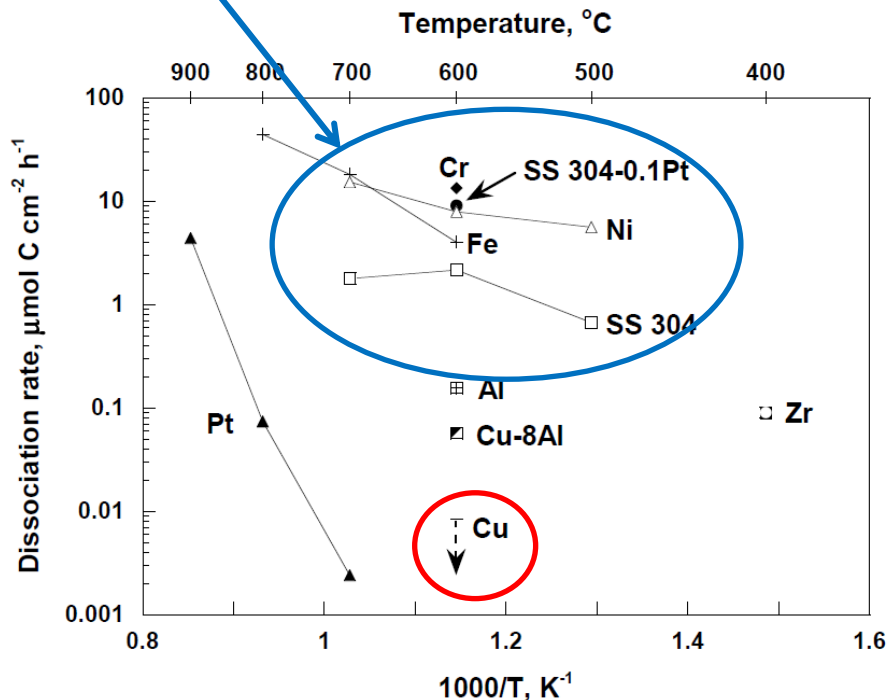


Fig. 10. Copper alloying effect on weight gain kinetics.

[Young et al. ECS Transactions, 16 (44) 3-15 (2009)]

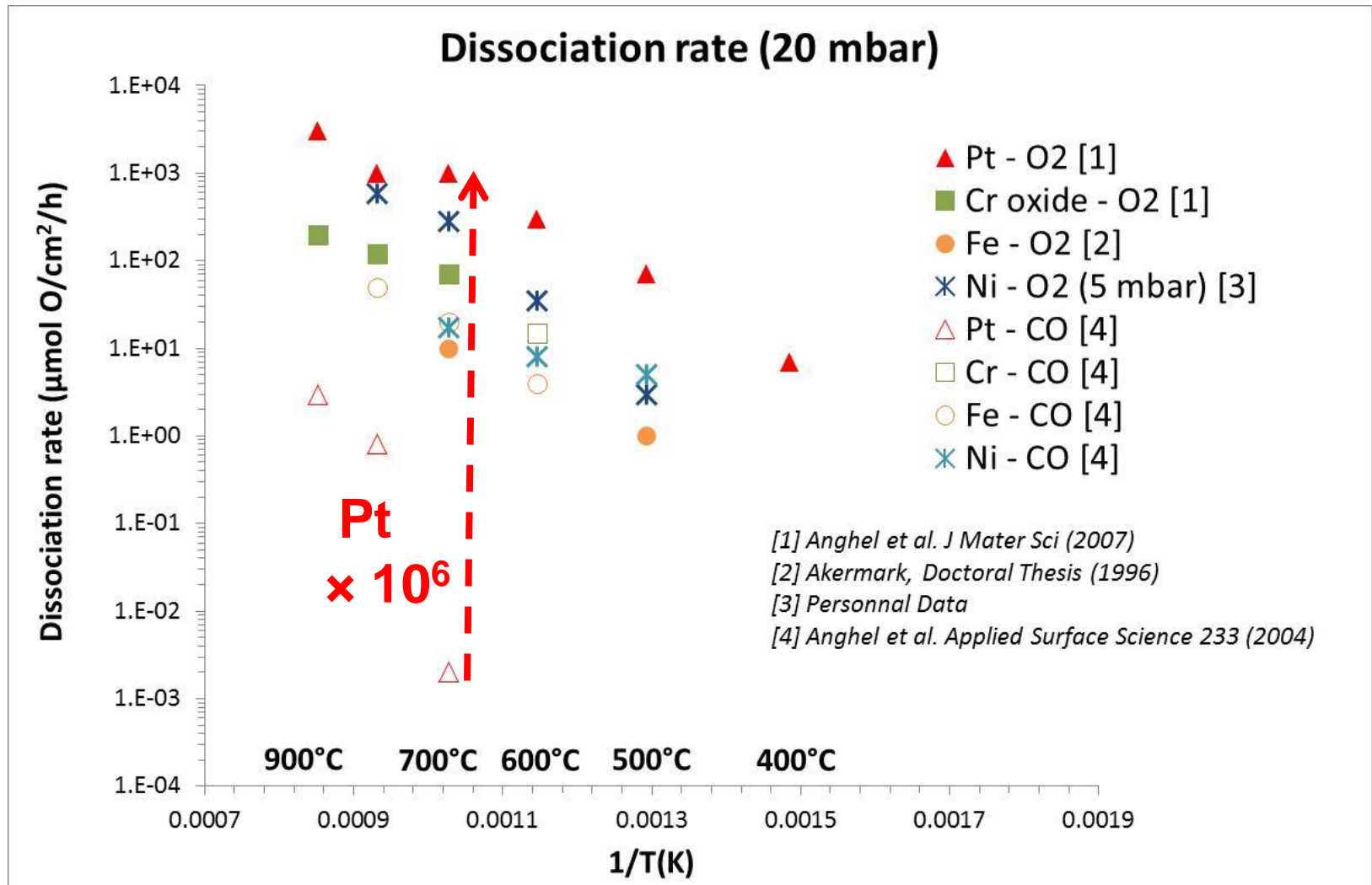
Fe, Ni, Cr dissociate well CO



[Anghel et al, Applied Surface Science 233 (2004)]

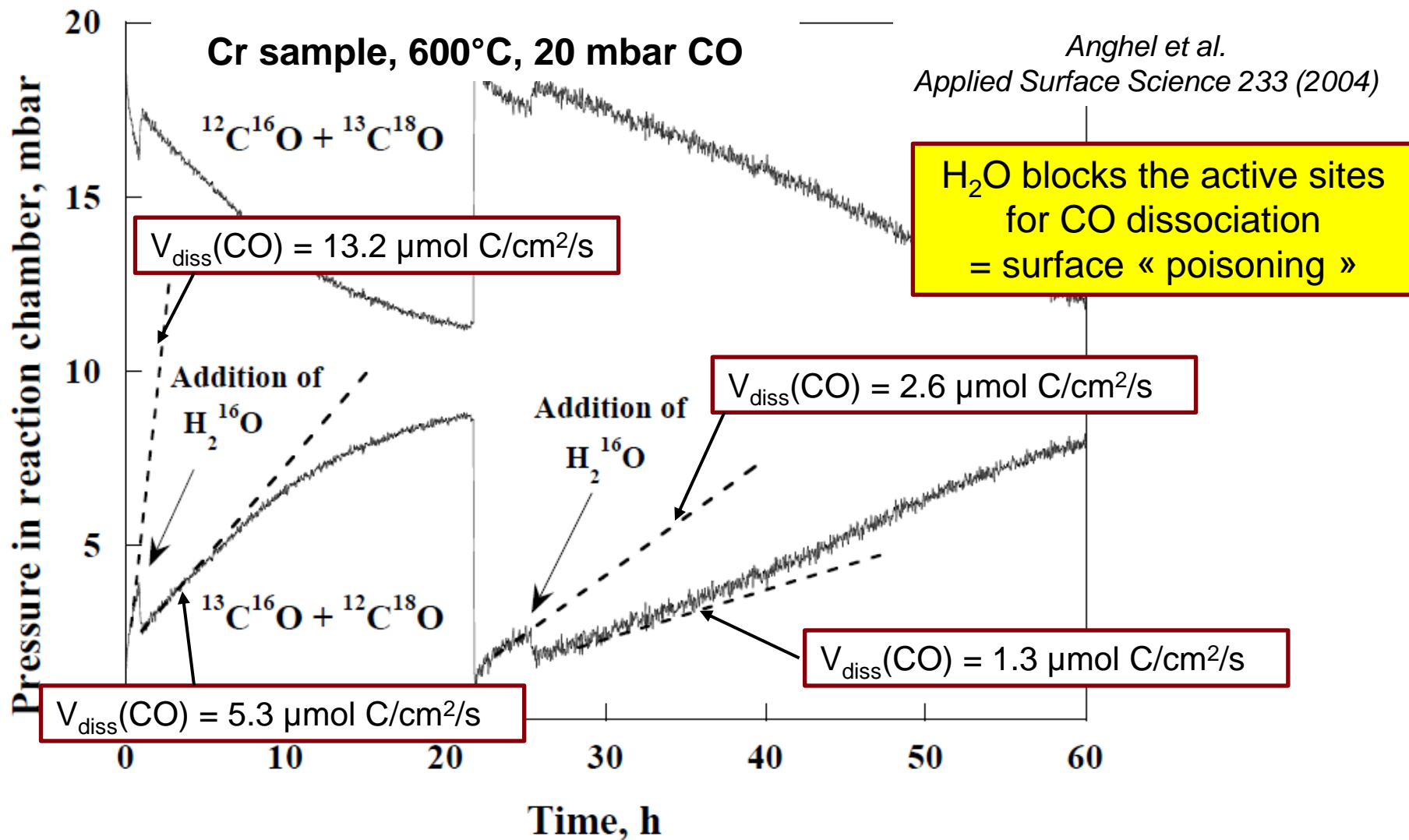
Possible explanation :
Cu does not dissociate well CO

DISSOCIATION RATES OF O₂ AND CO



Pt favors dramatically O₂ dissociation over CO dissociation :
alloy oxidation may be favoured over carburization when Pt deposit is applied

DEACTIVATION BY COMPETITIVE ADSORPTION



Confirmed by work on the oxidation of Cr-rich nickel base alloy in He with 130 μbar H_2 , 14 μbar CO and varying μbar H_2O at 850°C

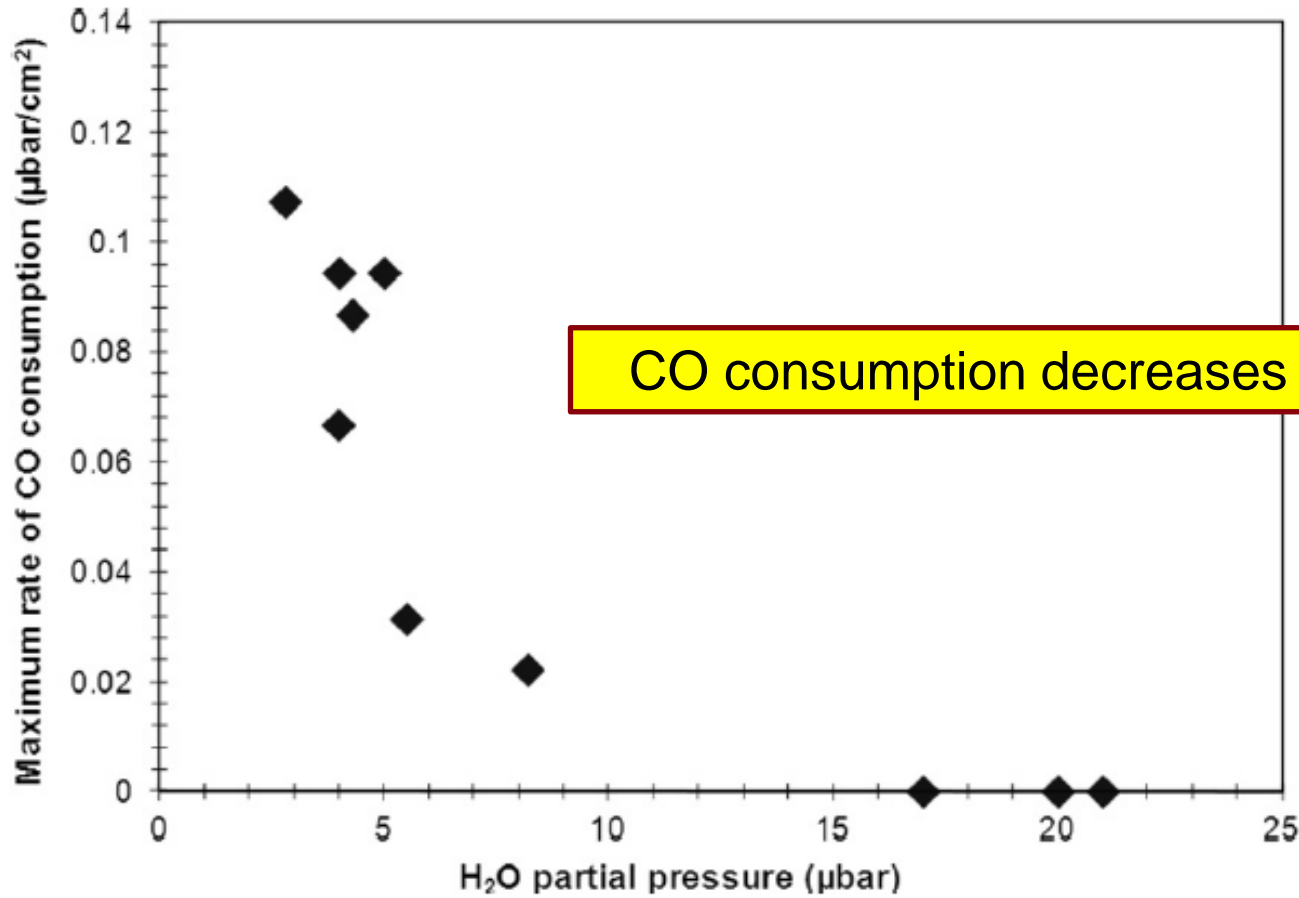
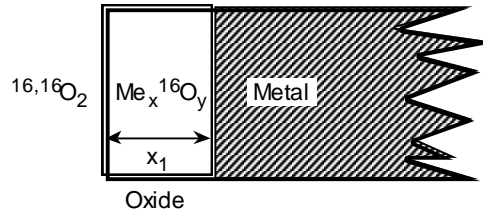


Fig. 6. Maximum CO consumption rate as a function of water partial pressure in He-14CO-130H₂.

CONSIDERATION OF OXYGEN EXCHANGE IN TWO-STAGE OXIDATION

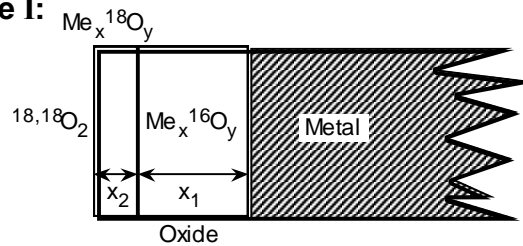
Stage one:



Akermark, Doctoral Thesis, 1996

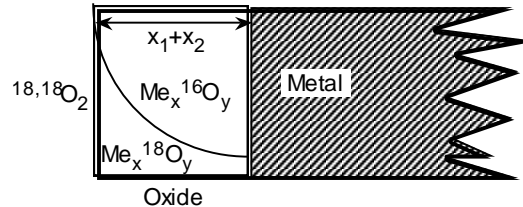
Stage two:

Case I:



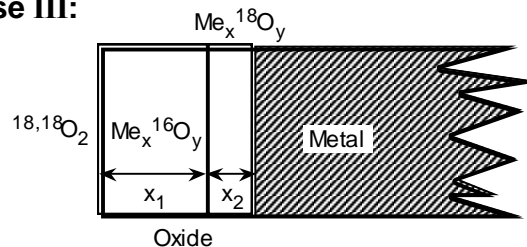
Oxide growth by Metal-ion transport

Case II:

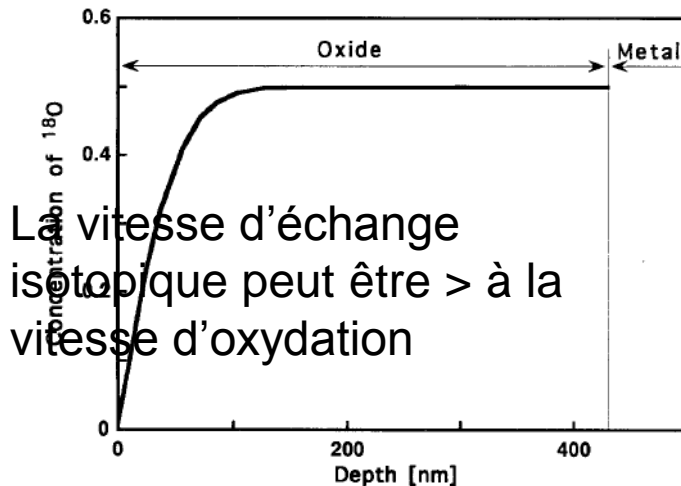
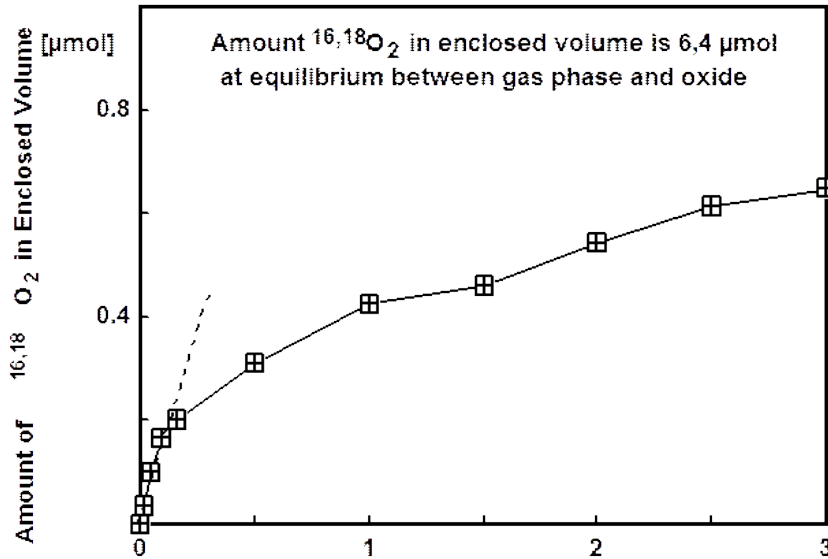


Oxide growth by Metal-ion and Oxygen transport

Case III:



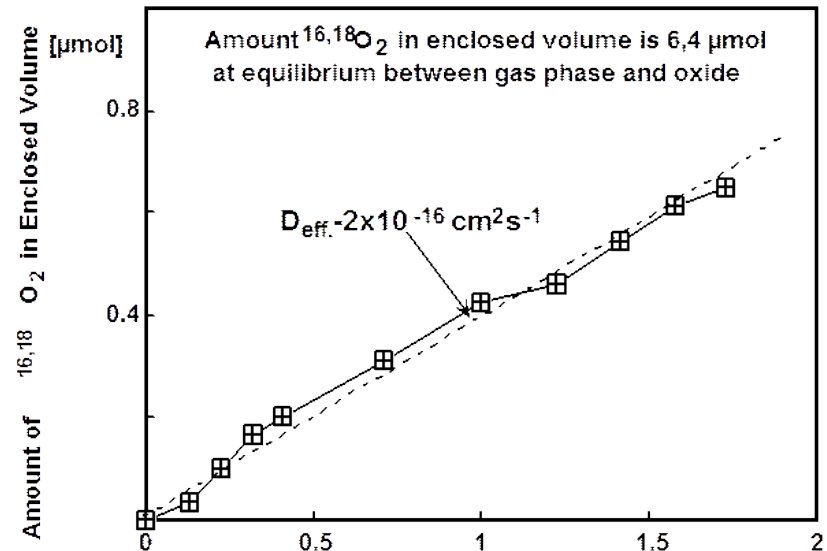
Oxide growth by Oxygen transport



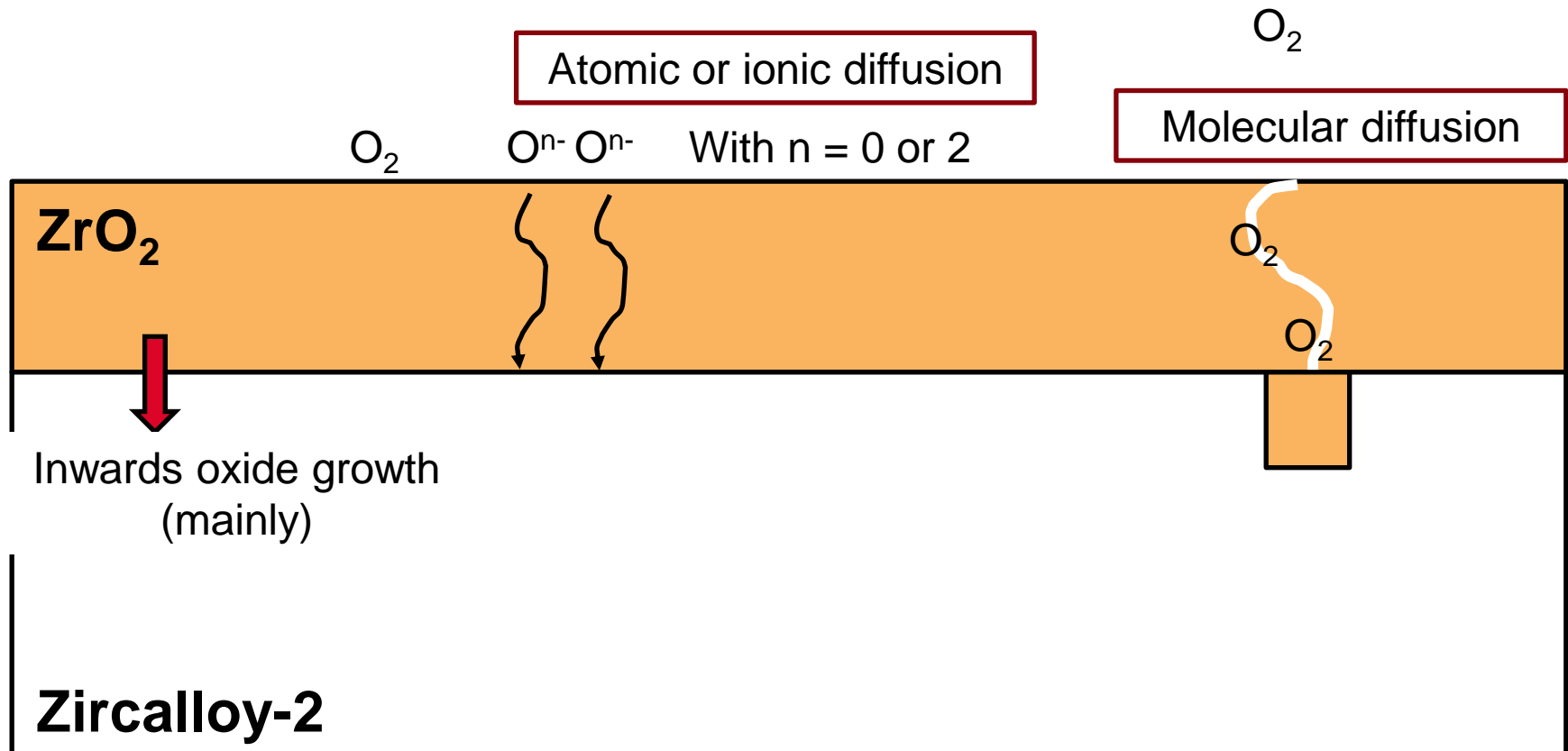
La vitesse d'échange isotopique peut être > à la vitesse d'oxydation

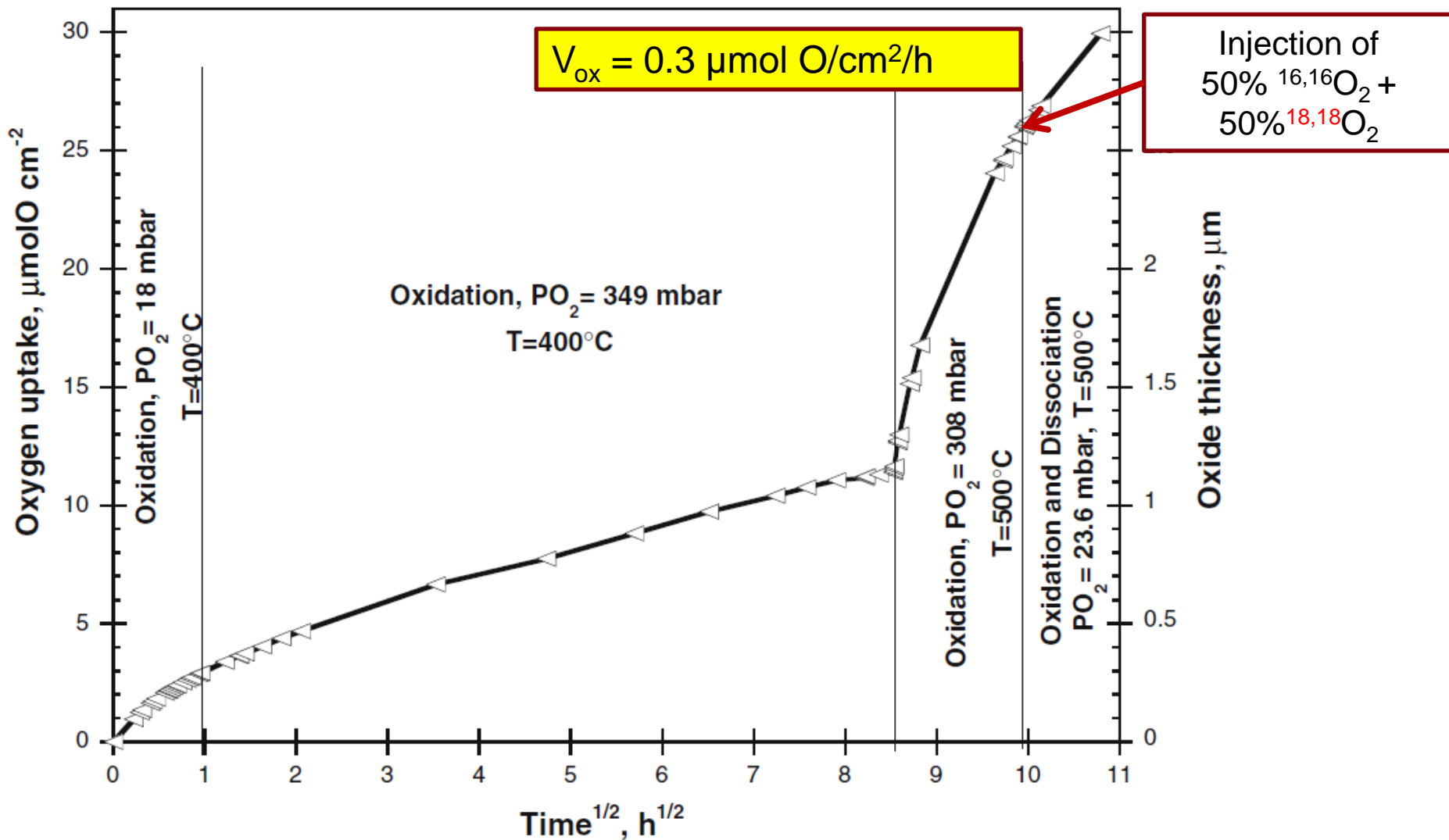
Fig. 14. Calculated depth profile of ^{18}O , $^{18}\text{O}/(^{16}\text{O}+^{18}\text{O})$, after oxidation of unannealed sample in 7.5 mbar O_2 (50% $^{16}\text{O}+50\%$ ^{18}O) for 47 h and then exposure to 7.5 mbar $^{16,18}\text{O}_2$ for 3 h at 920°C.

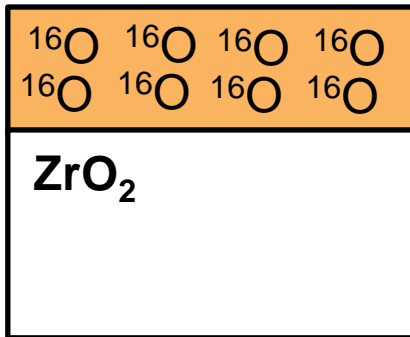
Amount of $^{16,18}\text{O}_2$ vs. time for an exposure to 7.5 mbar $^{16,18}\text{O}_2$ at 920°C of unannealed sample which previously was oxidised in 7.5 mbar O_2 (50% $^{16}\text{O}+50\%$ ^{18}O) for 47h



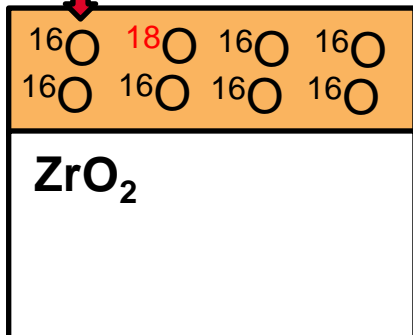
Il faut connaître l'épaisseur initiale
Article de Mishin et Borchardt J.
Phys. III France 3 (1993)







Hetero-exchange



$^{16,18}\text{O}_2$ is formed by homo and hetero-exchange = dissociation

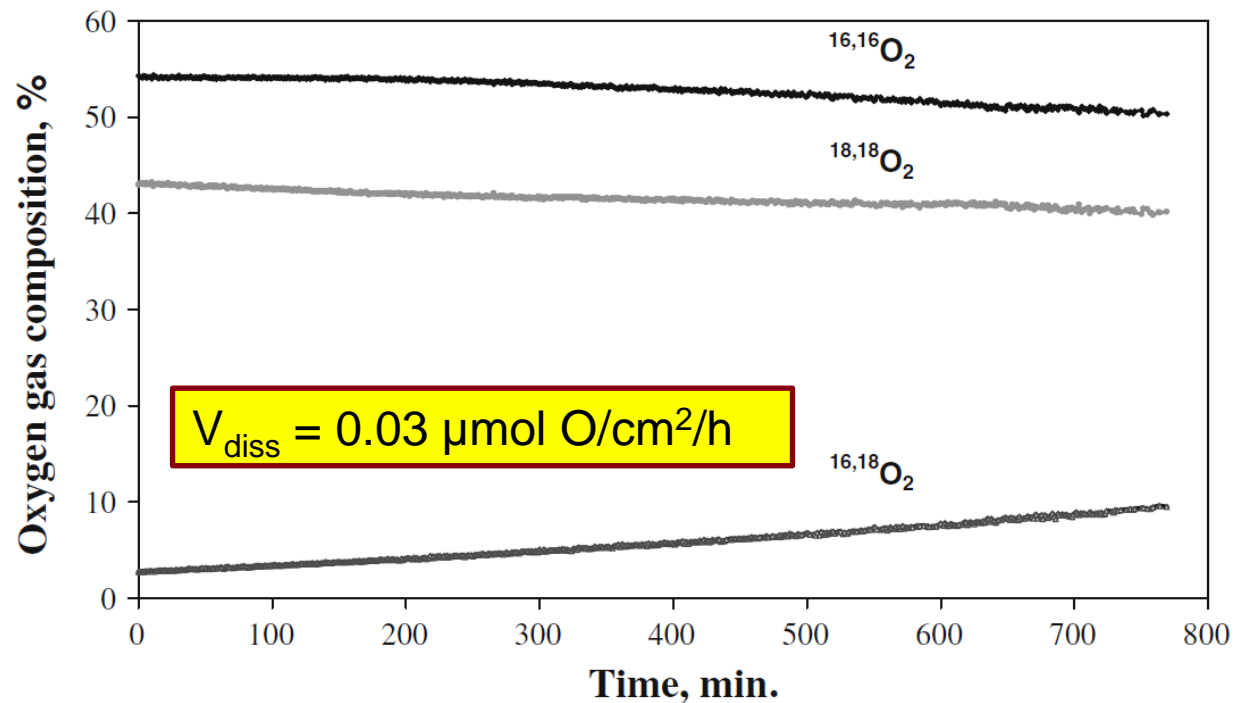


Fig. 10 Oxygen dissociation on preoxidized Zircaloy-2 at 500 °C in approximately 23.6 mbar O_2 (44.5% ^{18}O)

$$V_{\text{ox}} > 10 * V_{\text{diss}}$$

- Oxidation does not occur **only** by dissociated O on the oxide surface
- Direct access of molecular O₂ to the oxide/metal interface is necessary : existence of « open channels » in ZrO₂

GAS TRANSPORT IN OXIDE SCALE

DIFFUSIVITY AND PERMEABILITY IN OXIDE

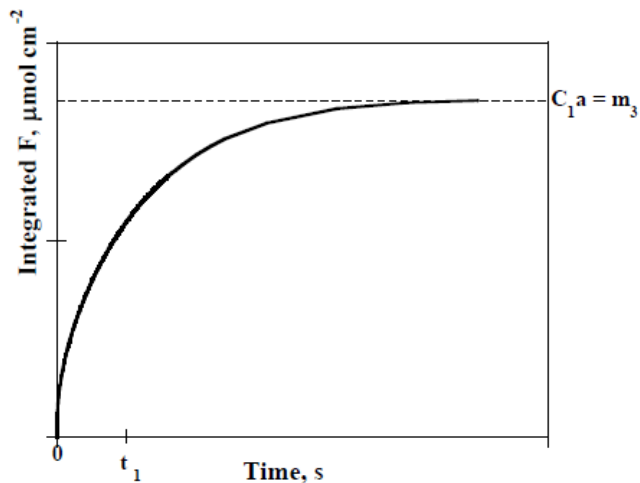
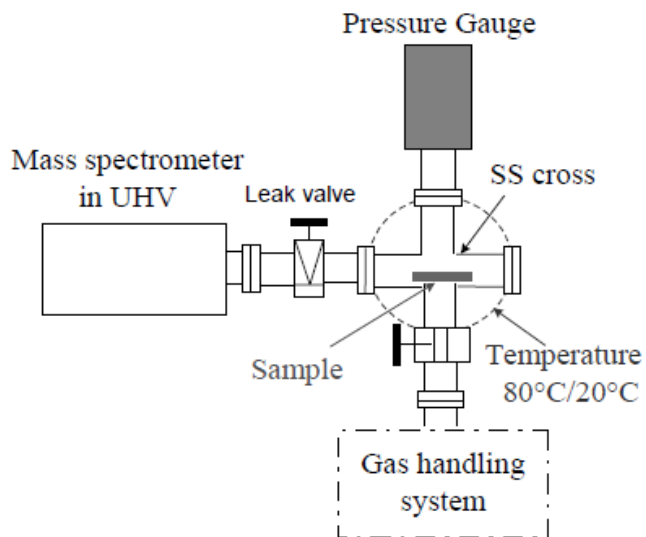


Figure 3. Integrated flux over time for an oxide scale of thickness a

Equilibration in air then outgassing

Data obtained :

Total concentration C_1 ($\mu\text{mol/cm}^3$)

Diffusivity D (cm^2/s)

$$F = \frac{2DC_1}{a} \sum_{n=1}^{\infty} \exp(-k_n^2 Dt)$$

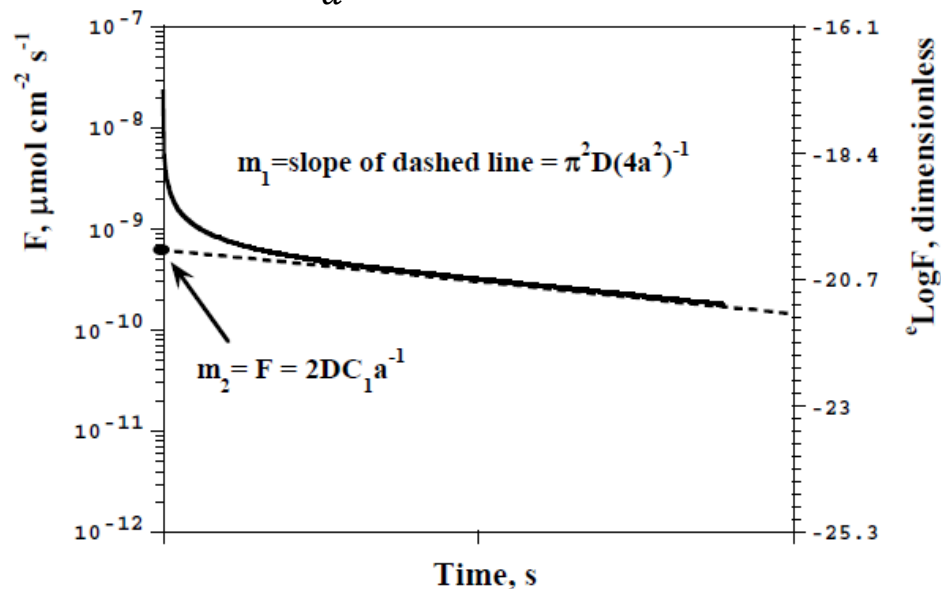


Figure 2. Flux versus time. The vertical axis has flux F with tick marks in powers of ten corresponding to the dimensionless scale $^{\circ}\text{log}F$.

DIFFUSIVITY IN ZR OXIDE

Anghel et al. Materials Science Forum Vols 522-523 (206) 93-102

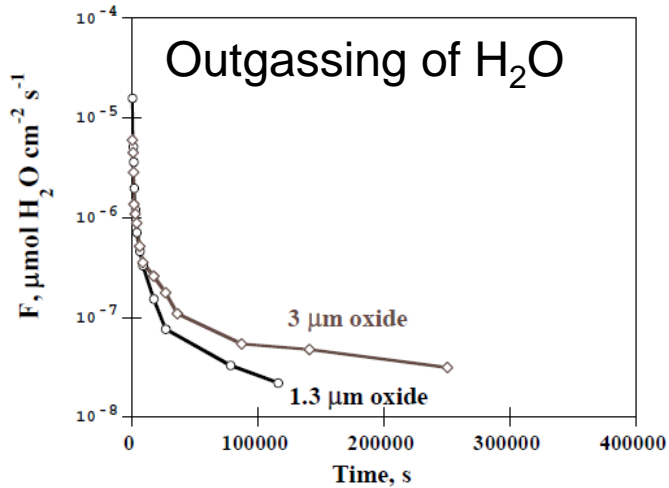


Figure 11a. Outgassing of H₂O from oxidized Zircaloy 2

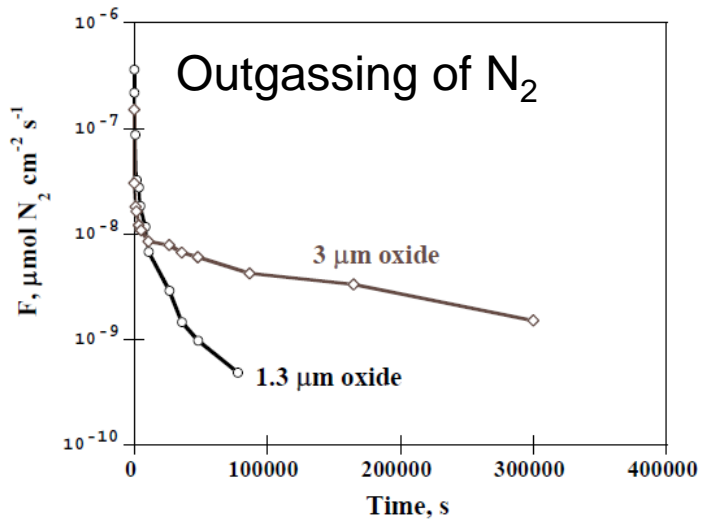
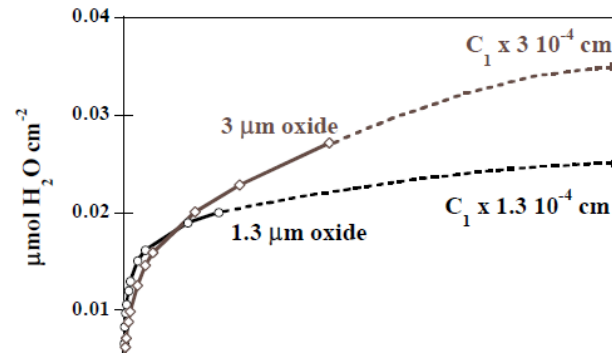


Figure 11b. Outgassing of N₂ from oxidized Zircaloy 2



Zr oxide	H ₂ O		N ₂	
Oxide thickness (μm)	1.3	3	1.3	3
Diffusivity (cm ² /s)	5.2 10 ⁻¹⁴	8.6 10 ⁻¹⁴	2.8 10 ⁻¹³	2.1 10 ⁻¹³
Concentration (μmol/cm ³)	190	119	3.8	5.0

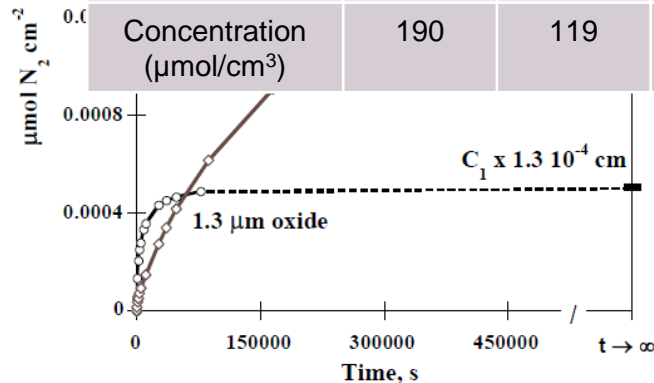
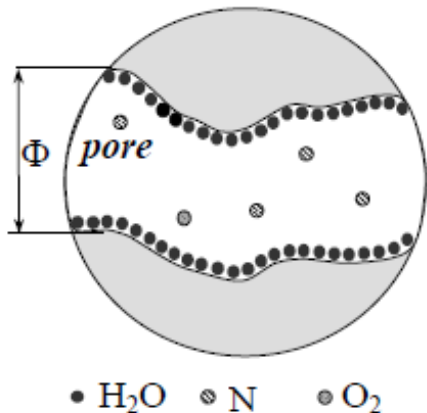
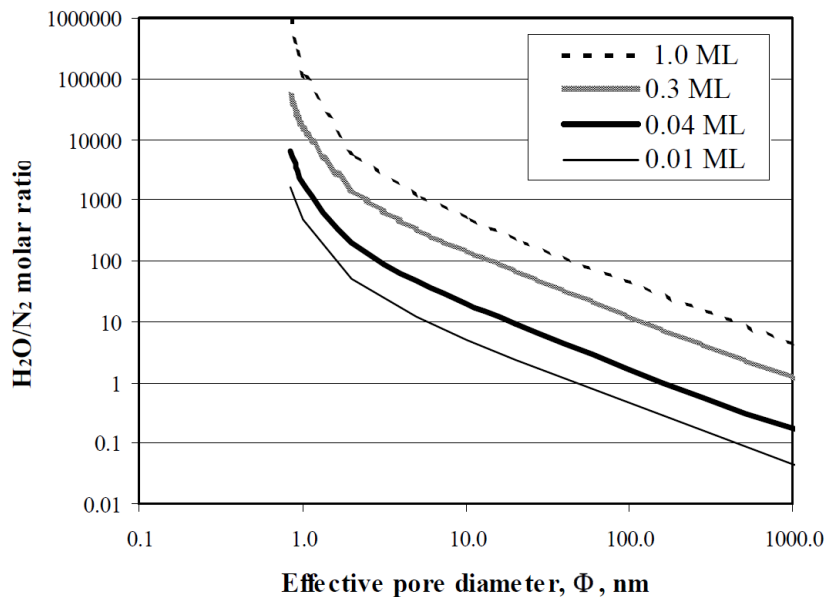


Figure 12b. N₂ integrated flux over time for Zircaloy-2 oxide scales

EFFECTIVE PORE SIZE



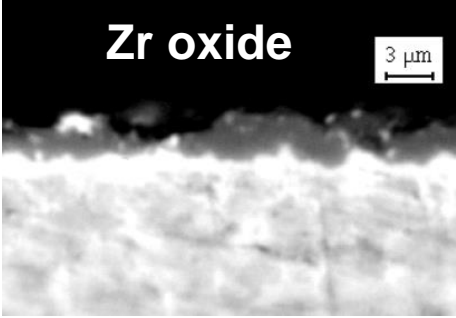
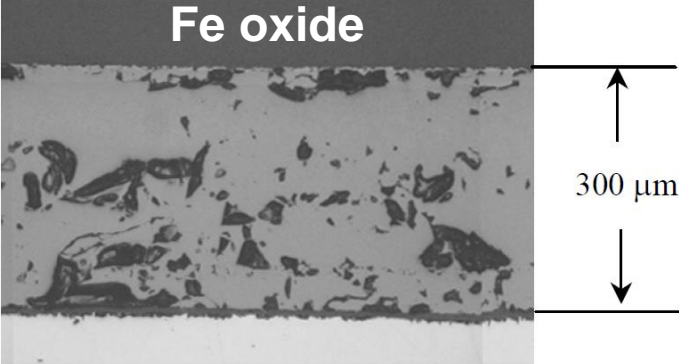
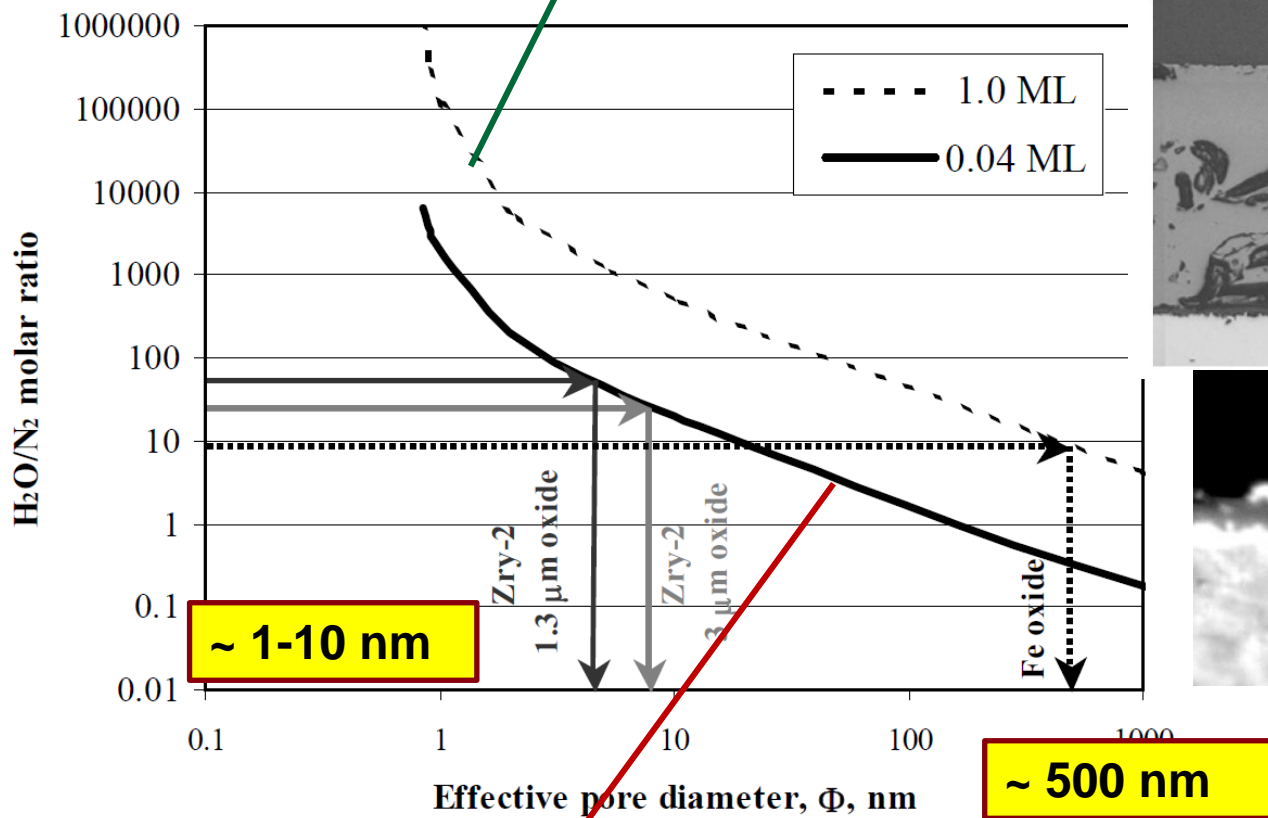
- ✓ Pore = long cylinder with circular cross section Φ
- ✓ H₂O adsorbs preferentially on the pore surface and H₂O in the gas phase is negligible
- ✓ Amount of N₂ released by outgassing → Total volume of the pores
- ✓ $n(\text{H}_2\text{O})/n(\text{N}_2)$ → Surface / Volume



Determination of the pore diameter based on known $n(\text{H}_2\text{O})/n(\text{N}_2)$ and water coverage

EXAMPLE ON ZR AND FE OXIDES

Fe oxide : water coverage = 1 ML and $n(\text{H}_2\text{O})/n(\text{N}_2) = 9$



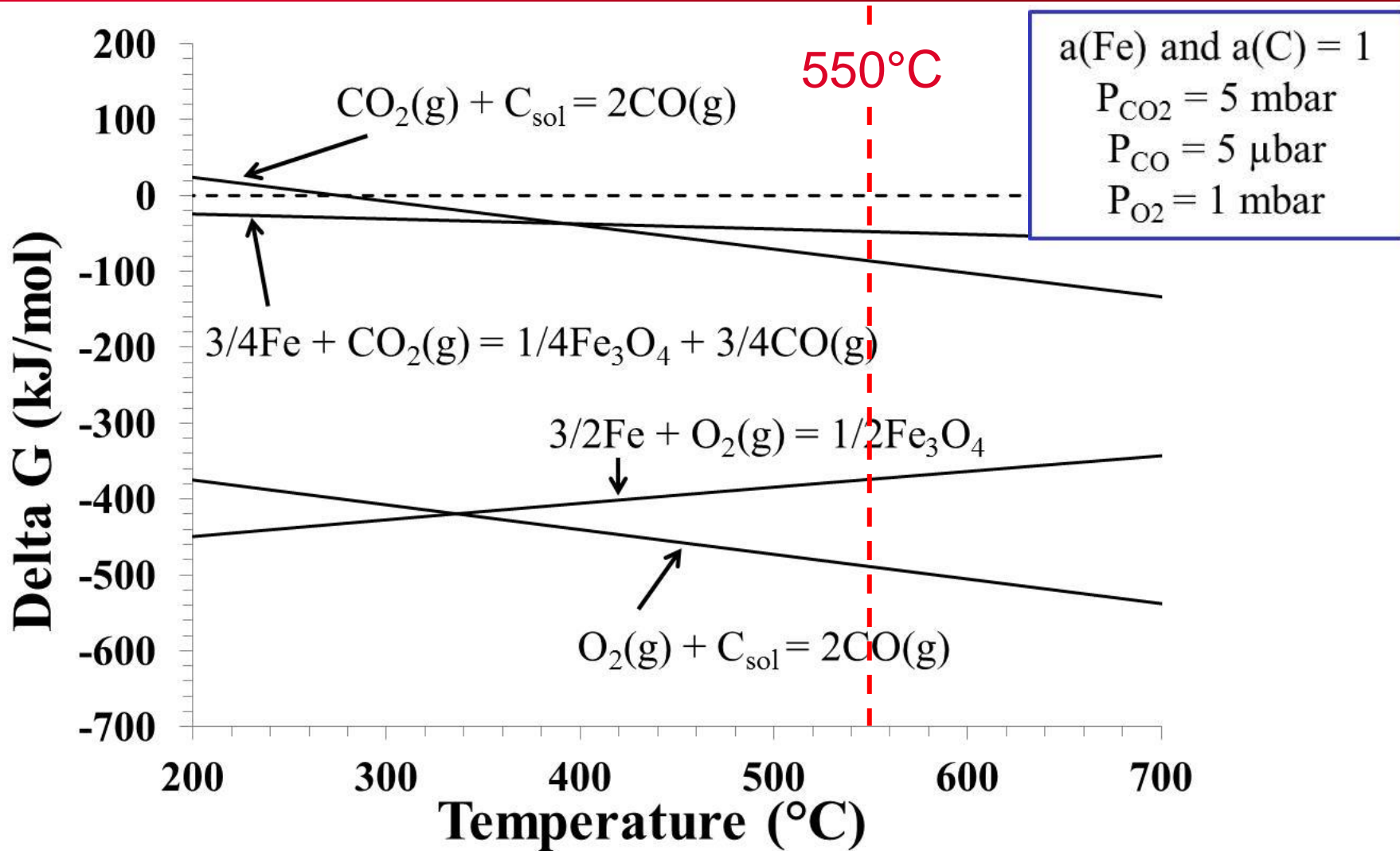
Zr oxide : water coverage = 0.04 ML and $n(\text{H}_2\text{O})/n(\text{N}_2) = 50$

REACTION MECHANISM IN MIXED ATMOSPHERES

MILD STEEL with :

- ❑ « pure » $^{13}\text{C}^{16,16}\text{O}_2$
- ❑ $^{13}\text{C}^{16,16}\text{O}_2$ with $^{18,18}\text{O}_2$

MILD STEEL IN « PURE » CO₂ - 550°C



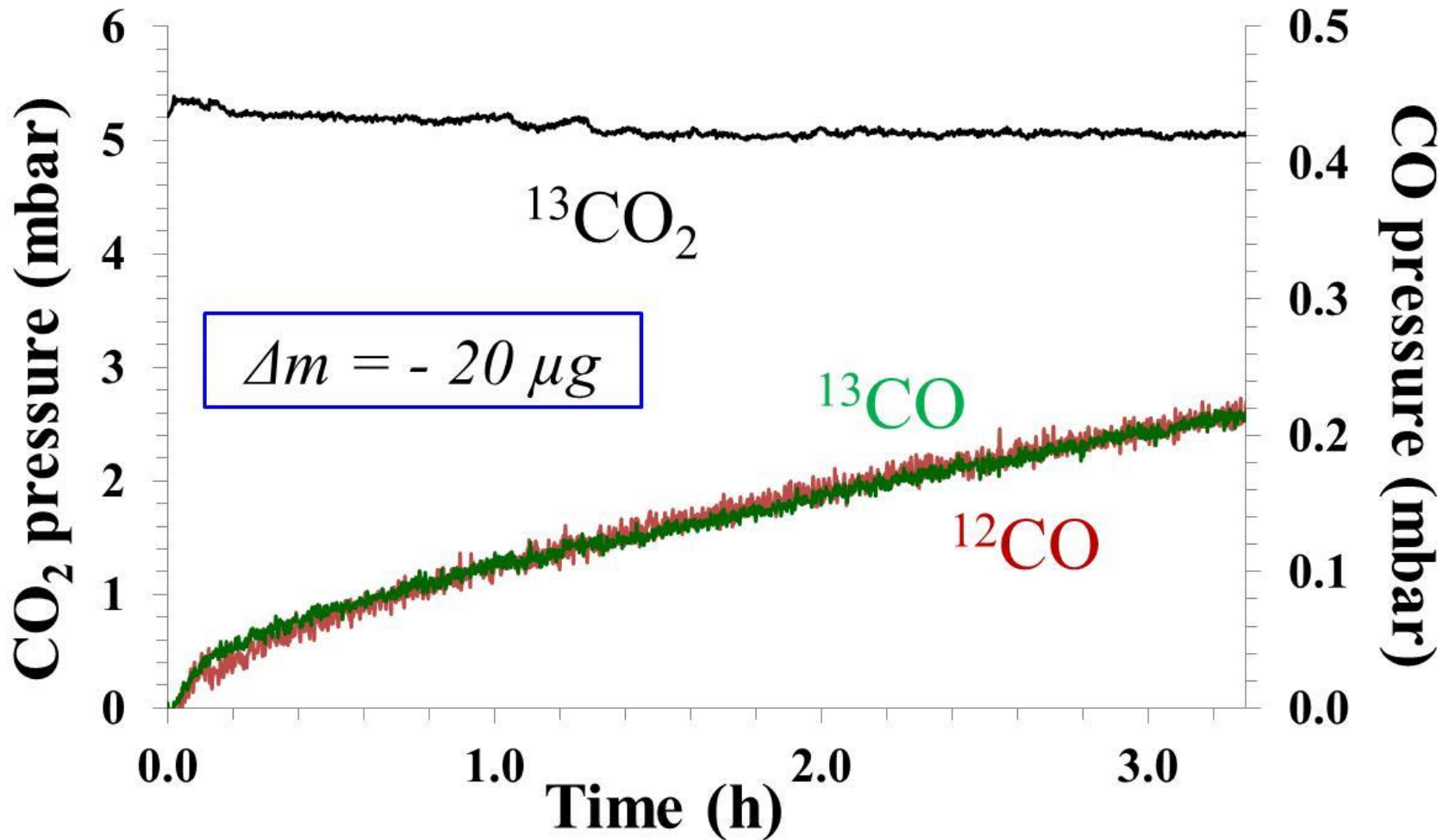
- With CO₂ and O₂, both oxidation and decarburization are possible at 550°C
- Both reactions are more favourable with O₂ than with CO₂ at 550°C

550°C, « instantaneous » temperature increase

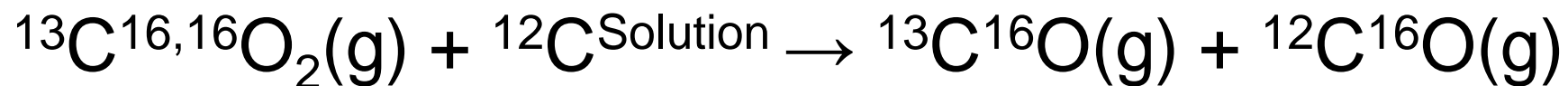
	¹³ C ^{16,16} O ₂	^{18,18} O ₂
Fe - 0.1%C	5 mbar	/

MILD STEEL IN « PURE » CO₂ - 550°C

- ❑ No oxidation but **decarburization** (CO release with ¹²C from Fe-C)
- ❑ In good agreement with metallic colored substrate and mass loss



Decarburization

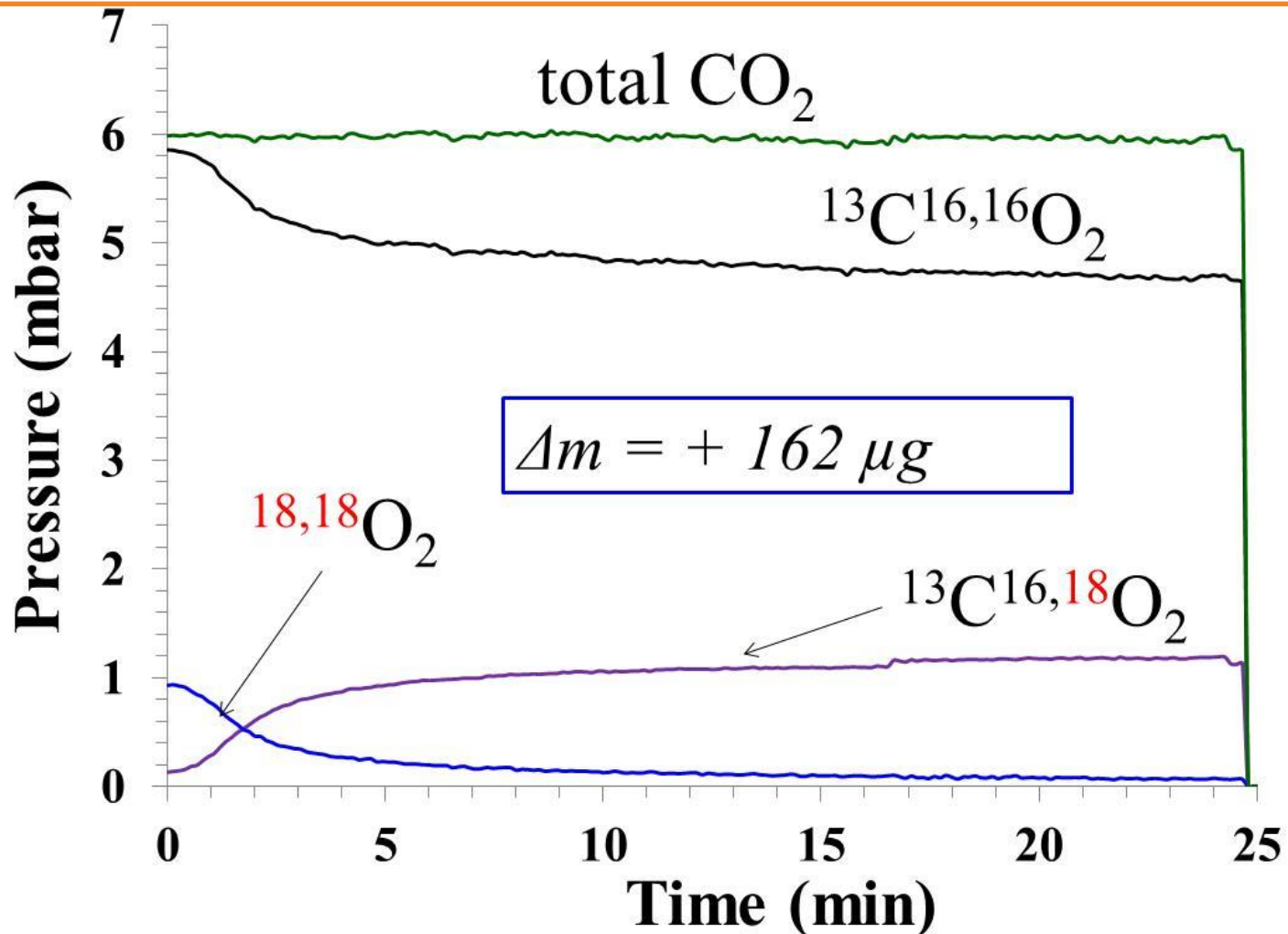


550°C, « instantaneous » temperature increase

Matériau	¹³ C ^{16,16} O ₂	^{18,18} O ₂
Fe - 0.1%C	5 mbar	1 mbar

MILD STEEL IN $\text{CO}_2 + \text{O}_2 - 550^\circ\text{C}$

- ❑ No decarburization and **very fast oxidation by O_2**
- ❑ In good agreement with dark colored substrate and mass gain
- ❑ No CO_2 consumption : only isotopic exchange with the oxide layer ?



Major reaction :



↓ ↓
Fe₃O₄ and Fe₂O₃
(Raman analysis)

The oxide layer formed by O₂(g) prevents decarburization

DRAGONS allow

CONCLUSIONS

- ❑ Using Gas phase analysis device such as DRAGONS help :
 - **Comparer le pouvoir dissociatif de matériaux vis-à-vis de molécules**
 - **Proposer un schéma réactionnel solide/gaz (couplage analyse gaz par SM / analyse solide par SIMS)**
 - **Etudier la désorption et la perméation**

- ❑ Avantage de l'installation :
 - **Utilisation de molécules à fort « coût » (isotopes) mais en petite quantité**

- ❑ Domaine d'étude :
 - **Corrosion**
 - **Catalyse**

THANK YOU ?

Any questions

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RESULTATS BIBLIOGRAPHIQUES

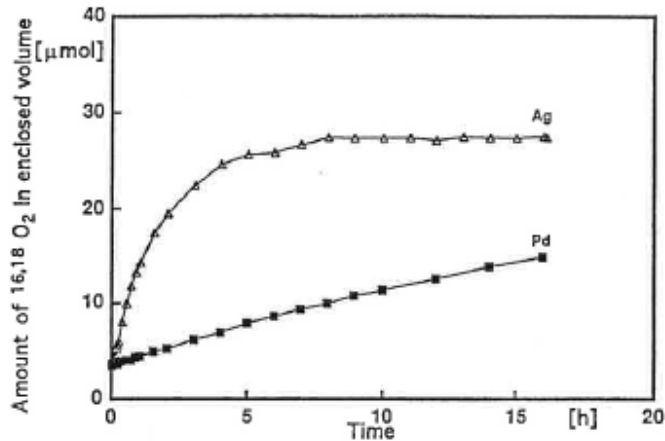


FIG. 6b. Increase of $^{16,18}\text{O}_2$ during exposure of Pd and Ag to 12.5 mbar $^{16,16}\text{O}_2$ and 12.5 mbar $^{18,18}\text{O}_2$ at 400°C.

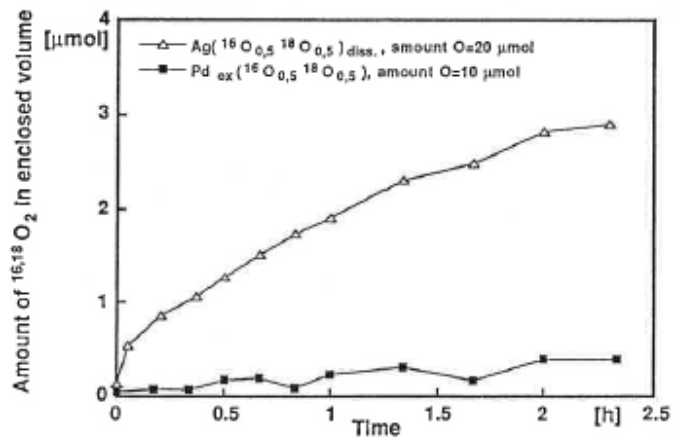


FIG. 6c. Exposure of Pd_{ex} and Ag(O)_{dis} to 35 μmol (13 mbar) $^{16,16}\text{O}_2$ at 400°C.

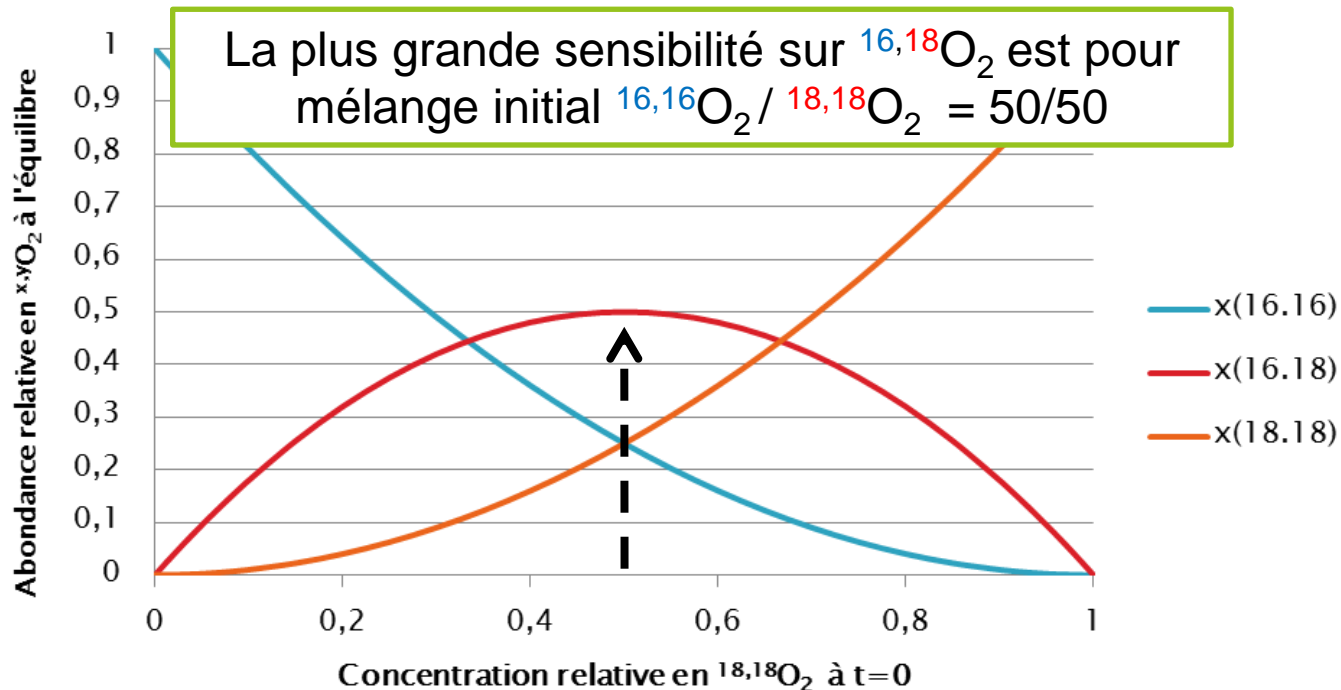
Akermark et al.
J Trace and Microprobe techniques,
14 (2) 1996

- Pd : échange gaz-oxyde négligeable
- Ag : échange gaz-oxygène dissous prépondérant

Probabilité de former une molécule $^{16,18}\text{O}_2$:

$$P^{16,18} = 2 \frac{[^{16}\text{O}] \times [^{18}\text{O}]}{([^{16}\text{O}] + [^{18}\text{O}])^2}$$

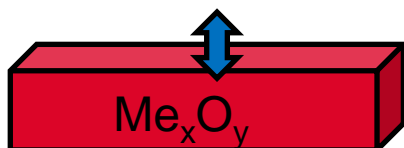
Indépendante de t



A SPECIFIC DEVICE BASED ON ISOTOPIC EXCHANGE



Exchange between O_2 on solid surface



Exchange between O_2 and $[\text{O}]$ from the oxide surface

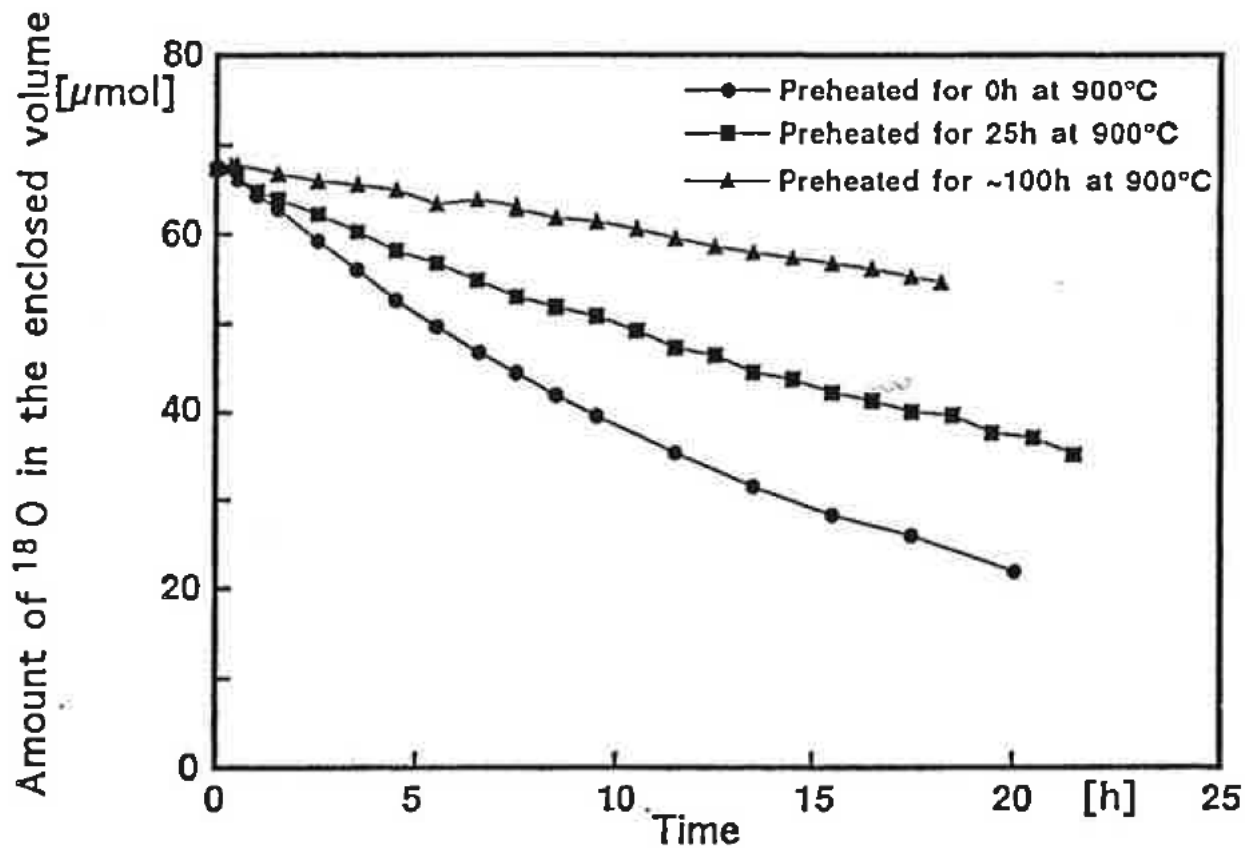


FIG. 7. Exposure of Y-doped Zr^{16}O_2 to 12.5 mbar $^{18,18}\text{O}_2$ at 900°C.