Aqueous Durability of Glasses – New Approaches

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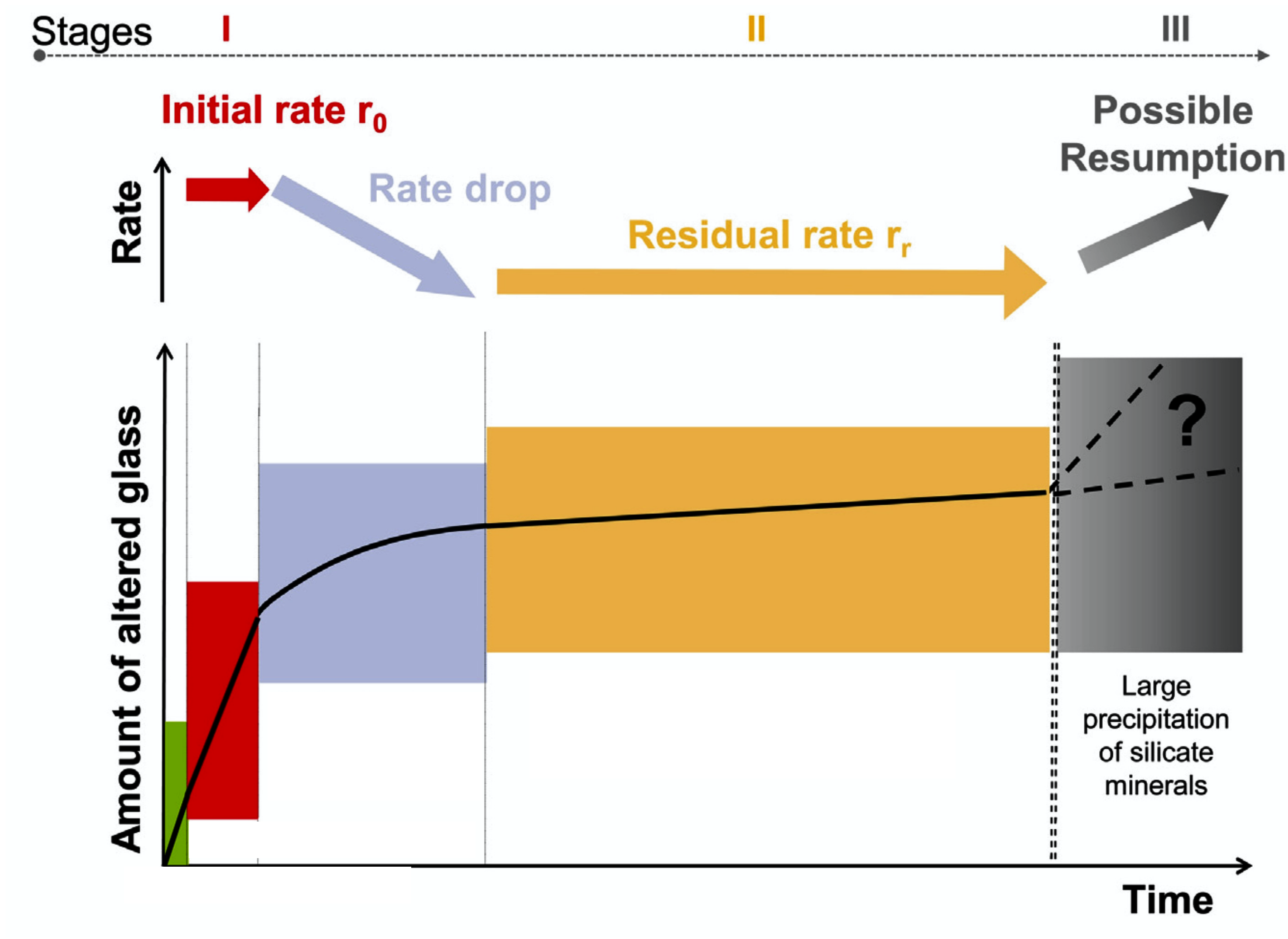
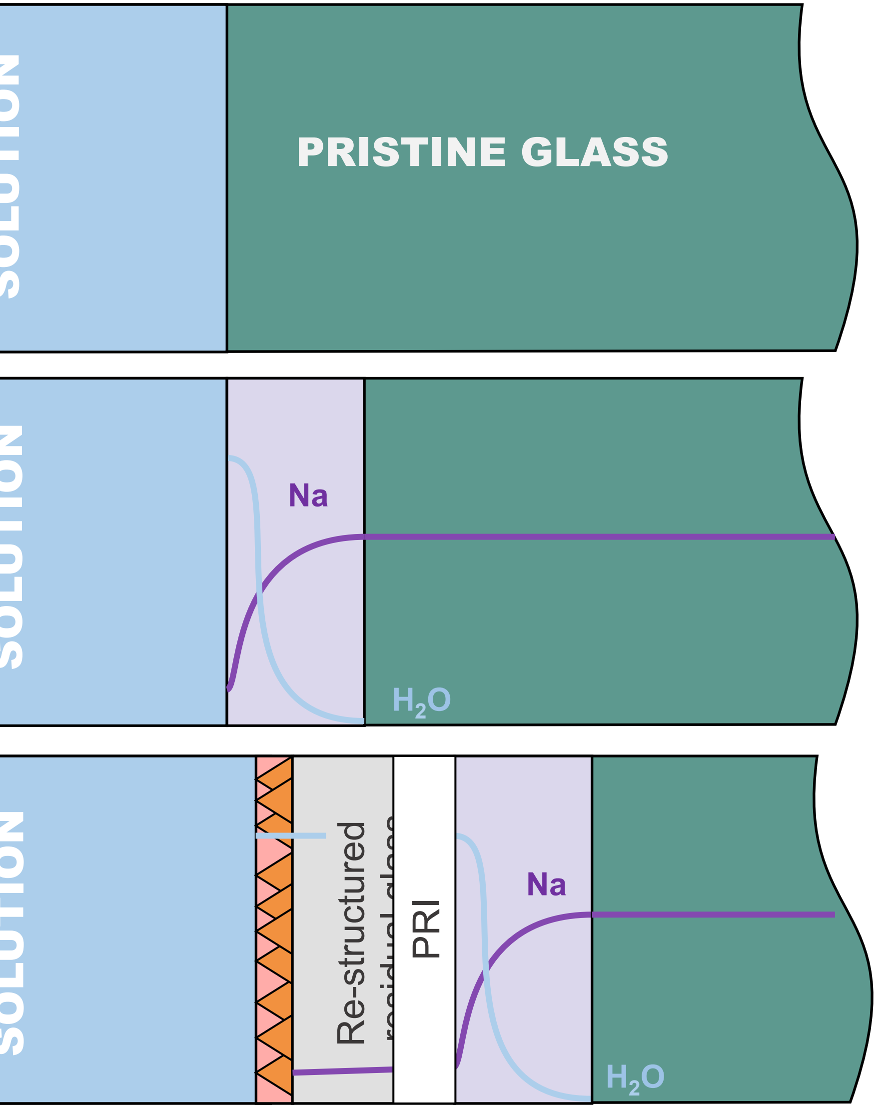
Observations: Corrosion kinetics

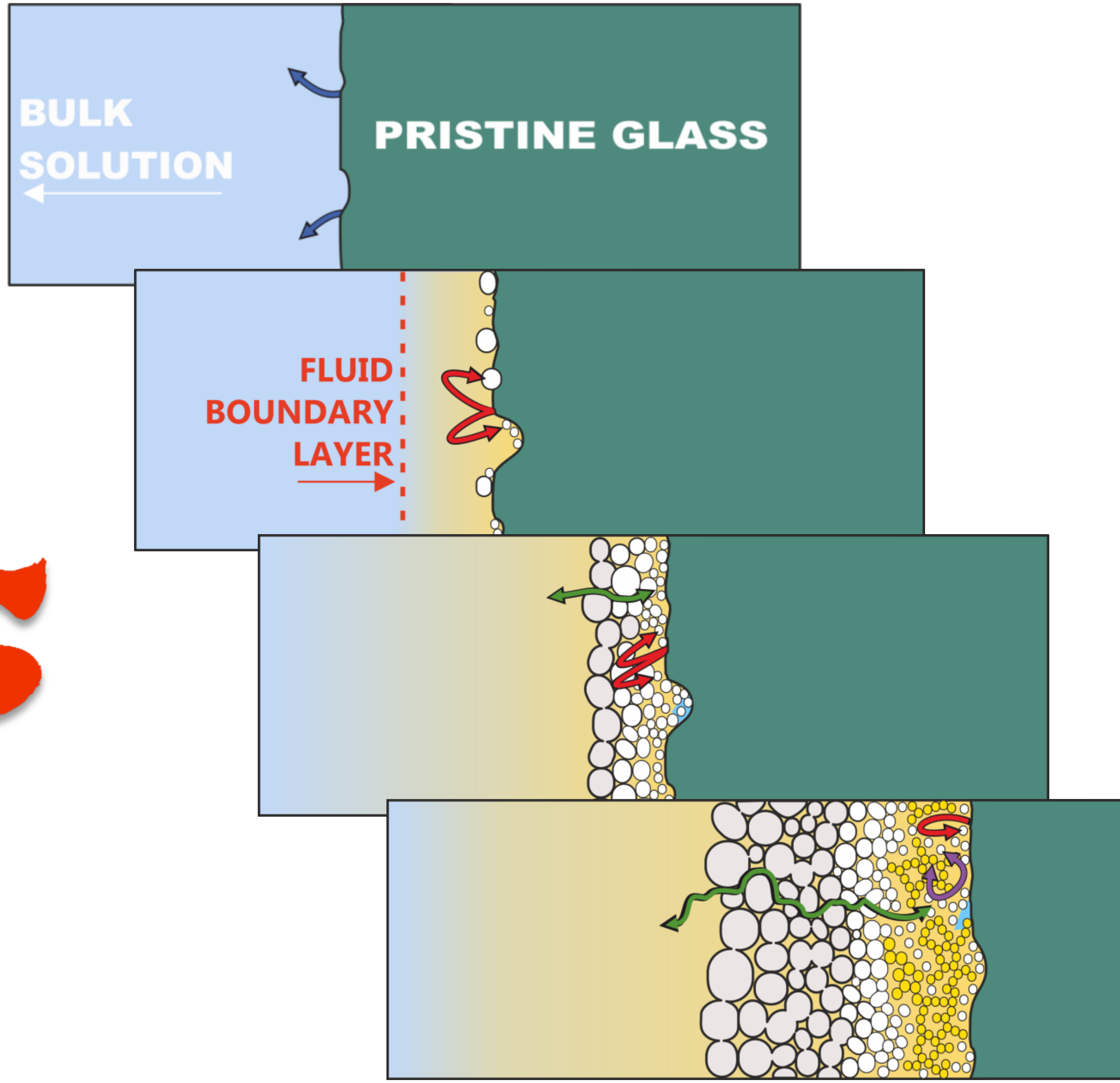


from Gin et al. (

Glass corrosion mechanisms

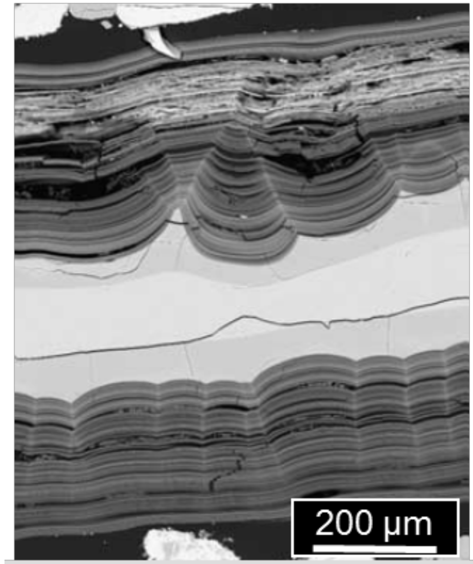


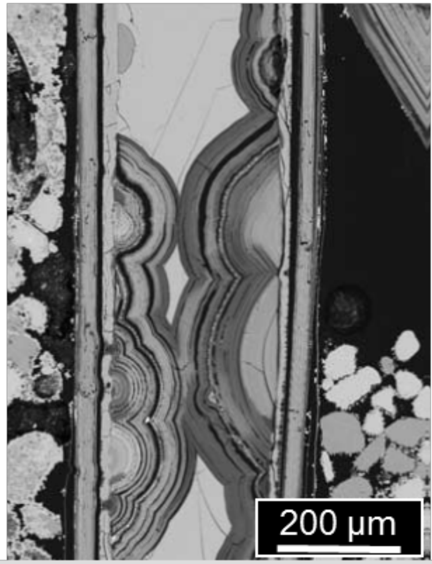
after Grambow (1986), Frugier et al. (2008)

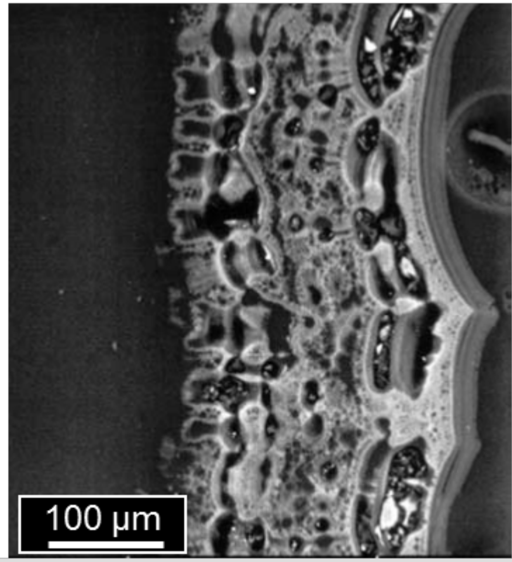


after Geisler et al. (2010; 20

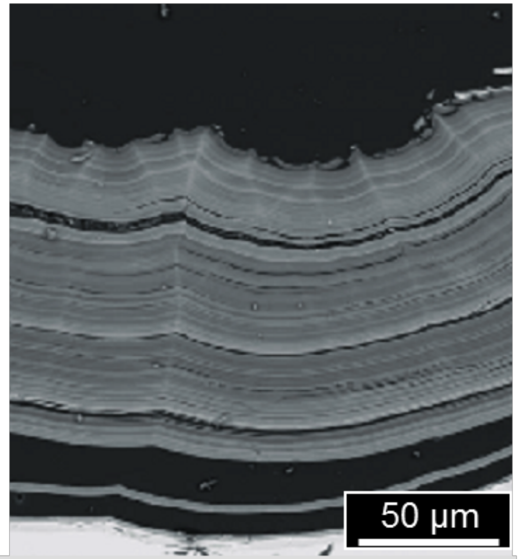
Observations – Patterned corrosion zones from nature



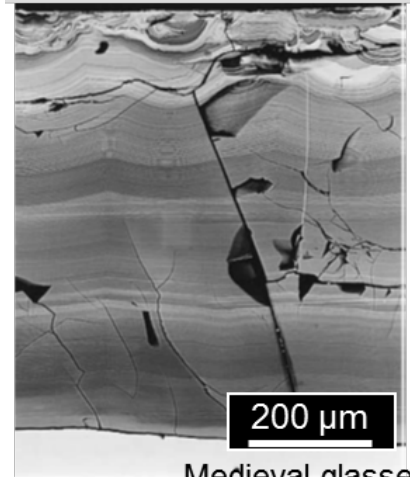


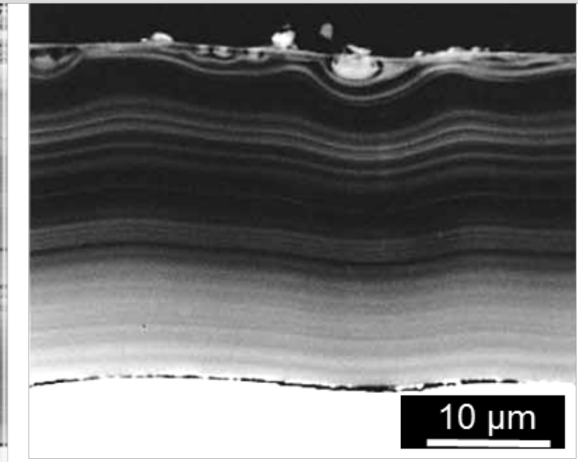


1800 yrs old glasses altered by sea and groundwater (Silvestri et al. 2005)

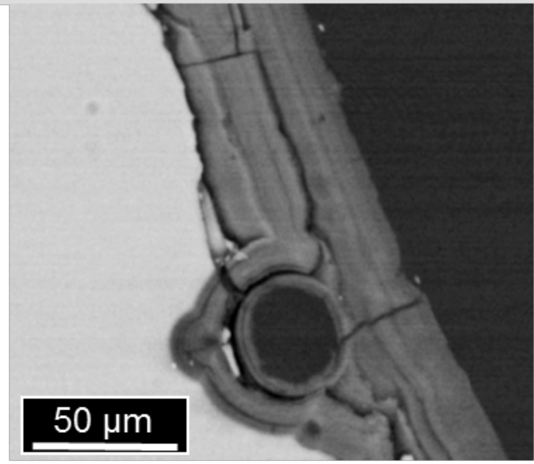


Medieval glass altered by groundwater (Geisler et al. 2010)

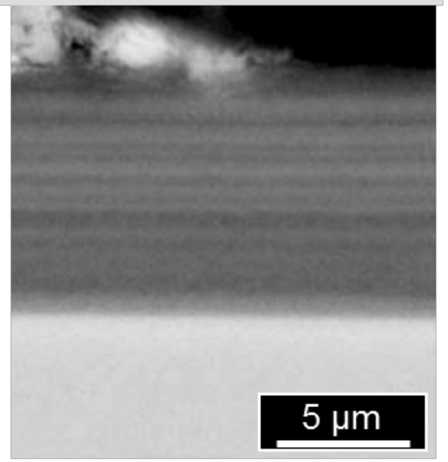




Medieval glasses altered by groundwater (Sterpenich & Libourel 2001)

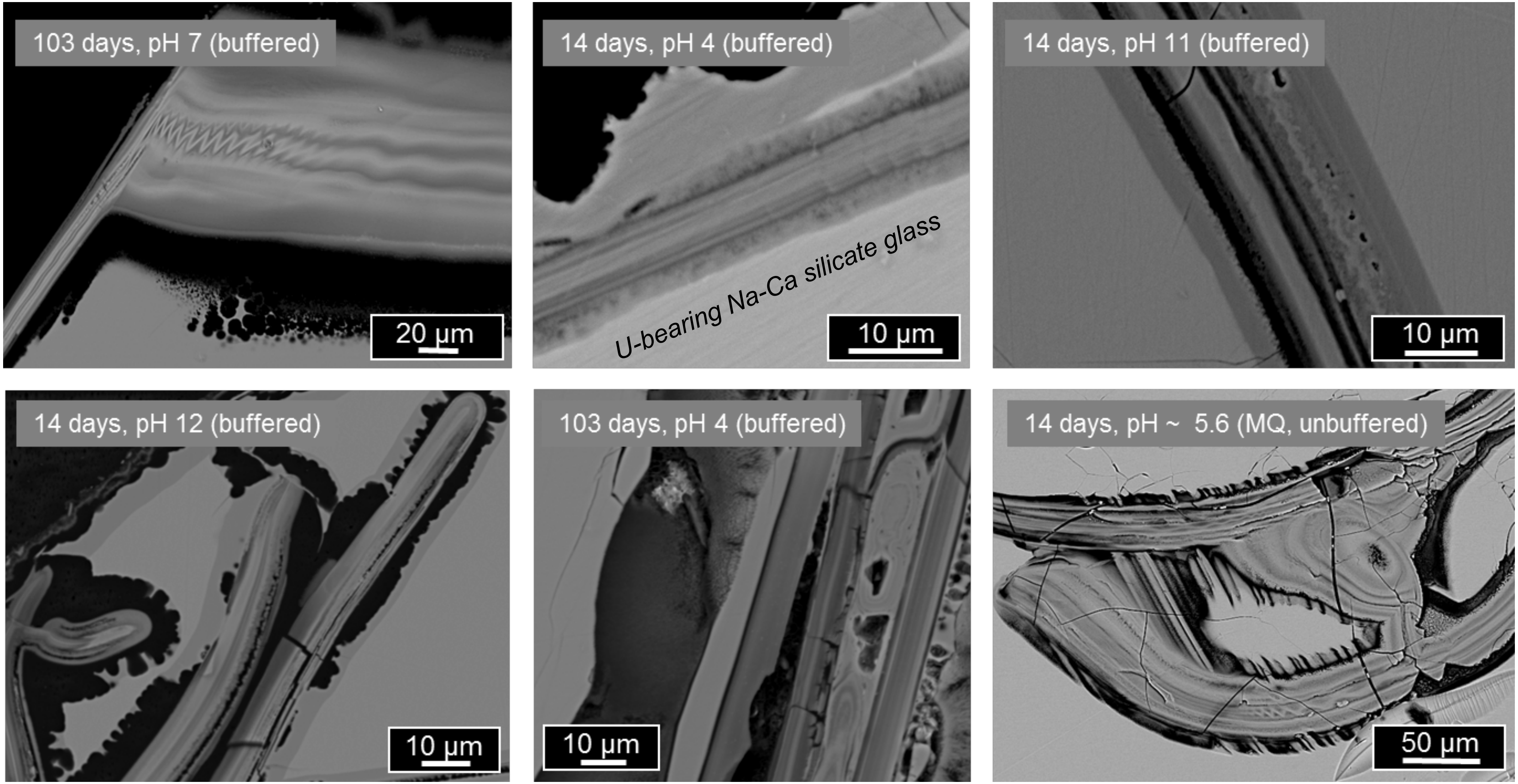


150 yrs old U-colored glass altered by groundwater (Prochazka 2007)



Glass buried for 9 years (McLoughlin et al. 2001)

Observations – Patterned corrosion zones from experiments



Dohmen et al. (2013)

Motivation

itations of and problems with the present experimental methodologies

lass-water reactions are commonly studied experimentally by *ex-situ* analysing the xperimental solution and/or reaction products, i.e., *after* the reaction has taken place.

mitations and problems of such an *ex-situ* approach are…

- short-time and small changes in the reaction kinetics are difficult to record
- quenching, drying, and physical sectioning may cause:
    - phase precipitation
    - structural and chemical changes of the reaction products
    - physical cracking

Motivation

itations of and problems with the present experimental methodologies

llows that

rmation about the dynamics of the structural and chemical evolution of the corrosion la

ot directly *accessible*. However, …

“a process cannot be understood by stopping it.
Understanding must move with the flow of the process, must join it and flow with it.”

— Frank Herbert, D

at can we do to overcome such limitations?

(Multi-)isotope tracer exchange experiment → isotope coupling or decoupling in spa and time gives information about the dynamics of individual reactions.

***In-situ* experiments** → following the reaction in real-time without disturbing it.

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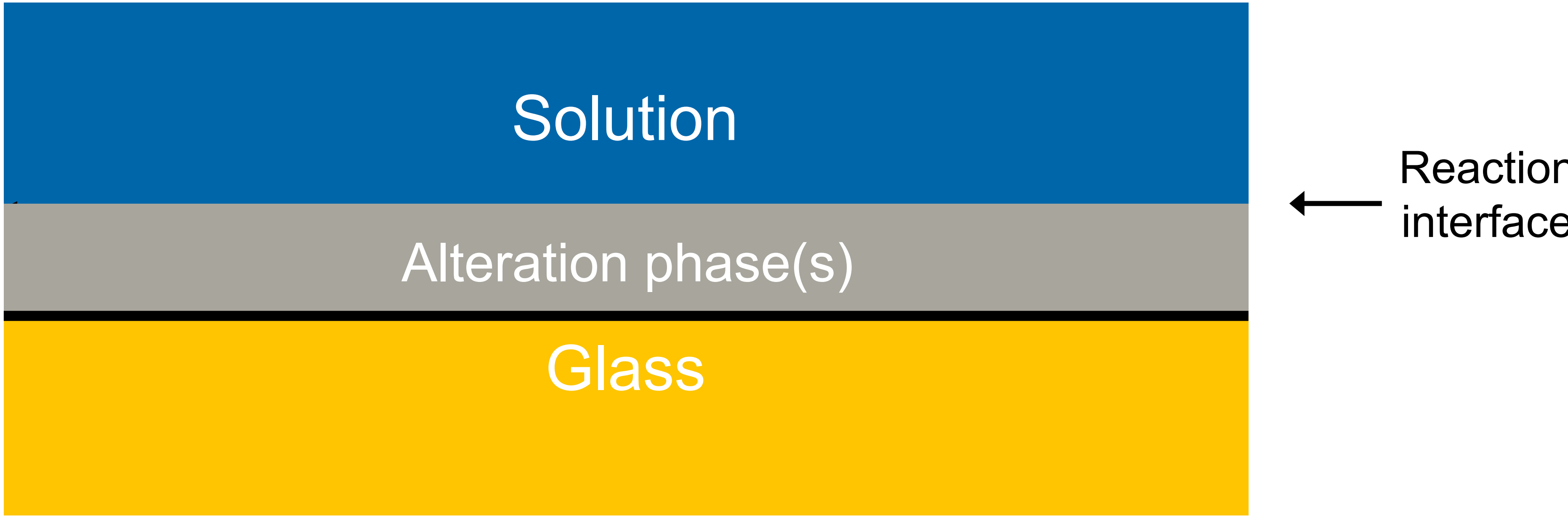
In-situ experiments

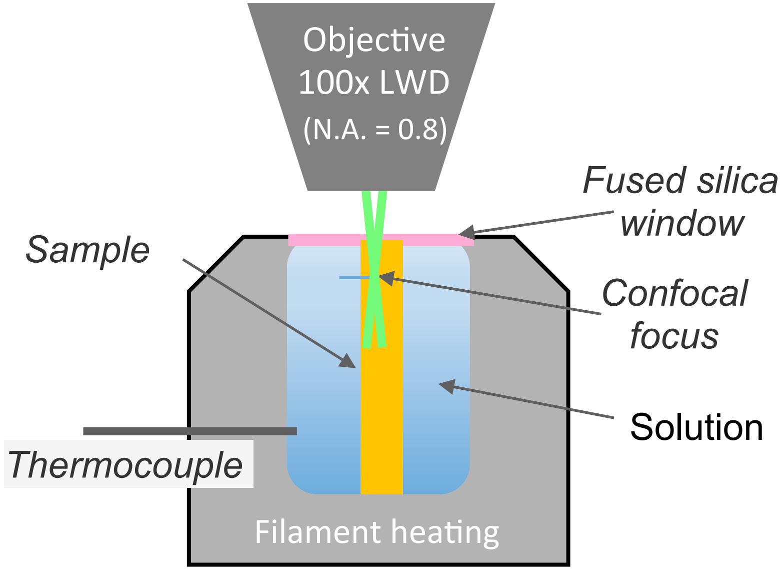
rrently established *in situ* techniques only probe surface reactions

(e.g., atomic force microscopy or interferometry)



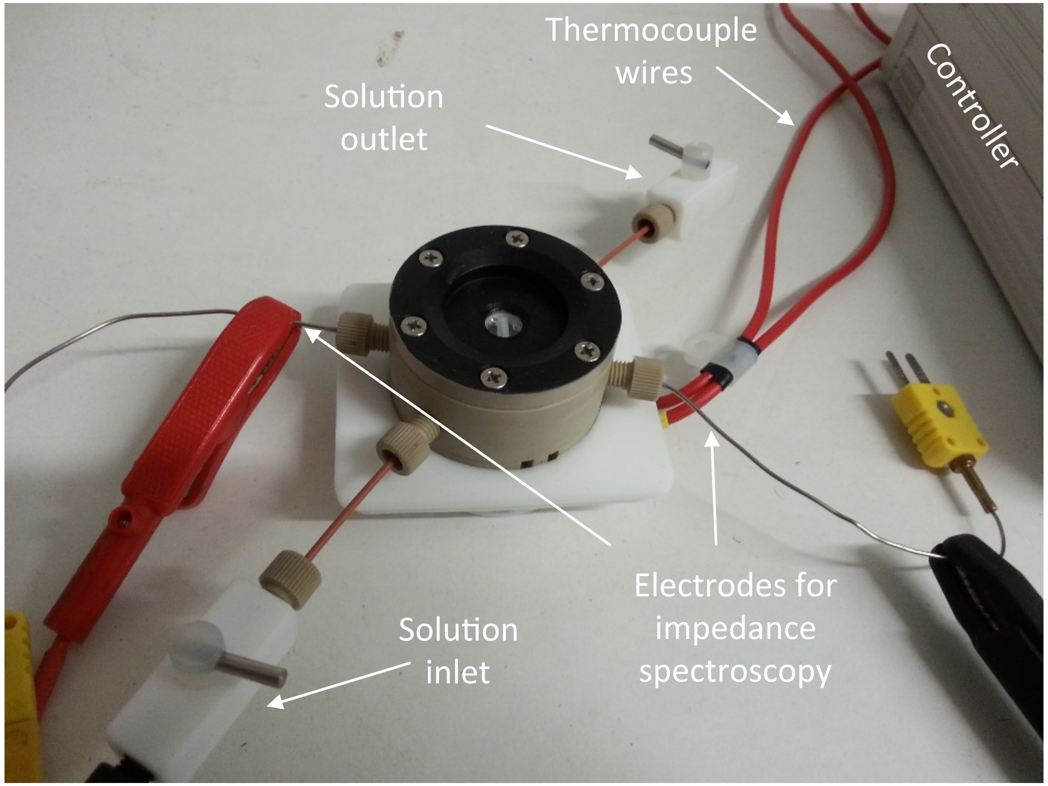
Experimental details

nfocal Raman spectroscopy allows overcoming such limitations



T = 70 and 90°C, 26 to 240 h

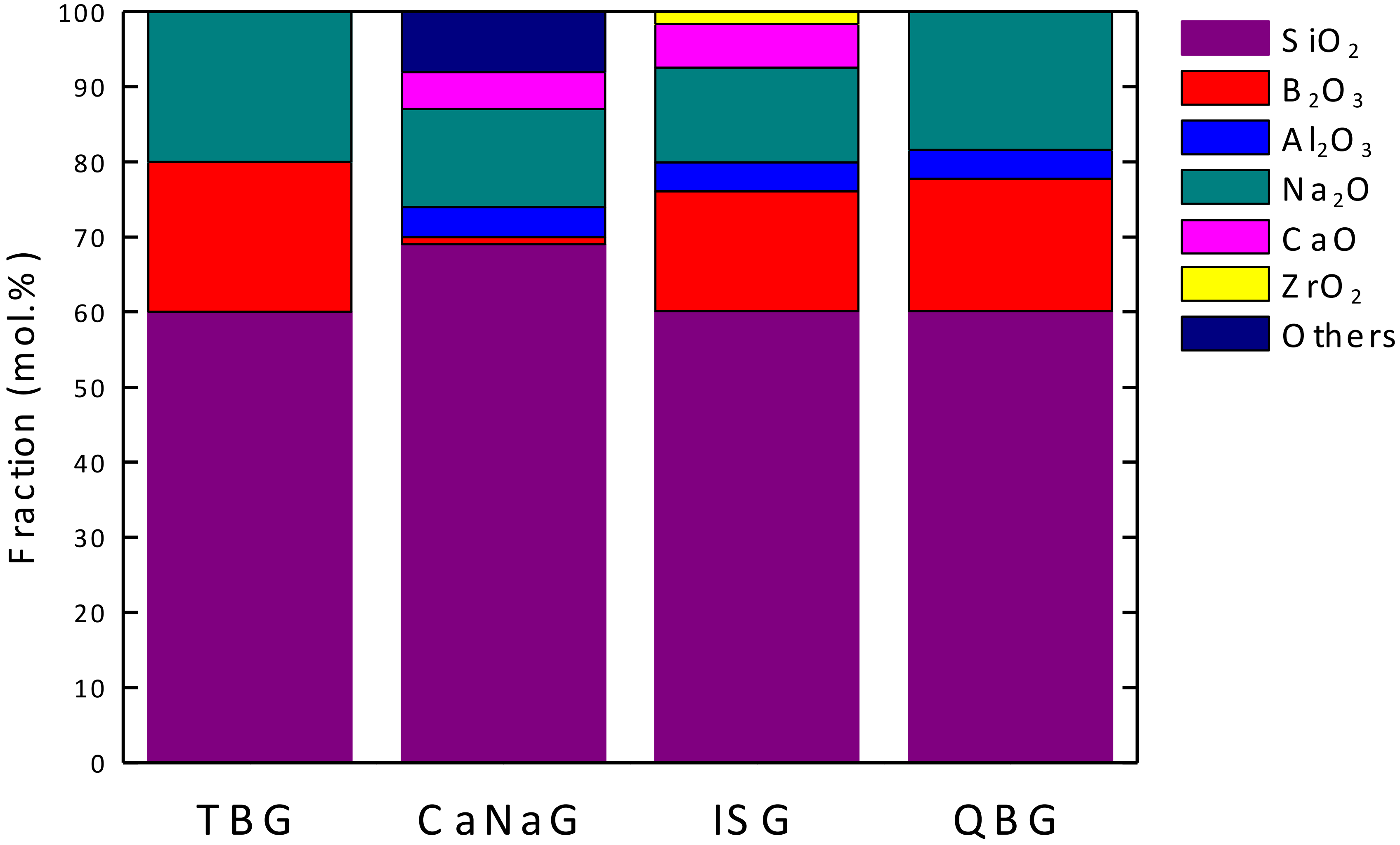
Schematic Raman fluid cell setup



Raman fluid cell setup

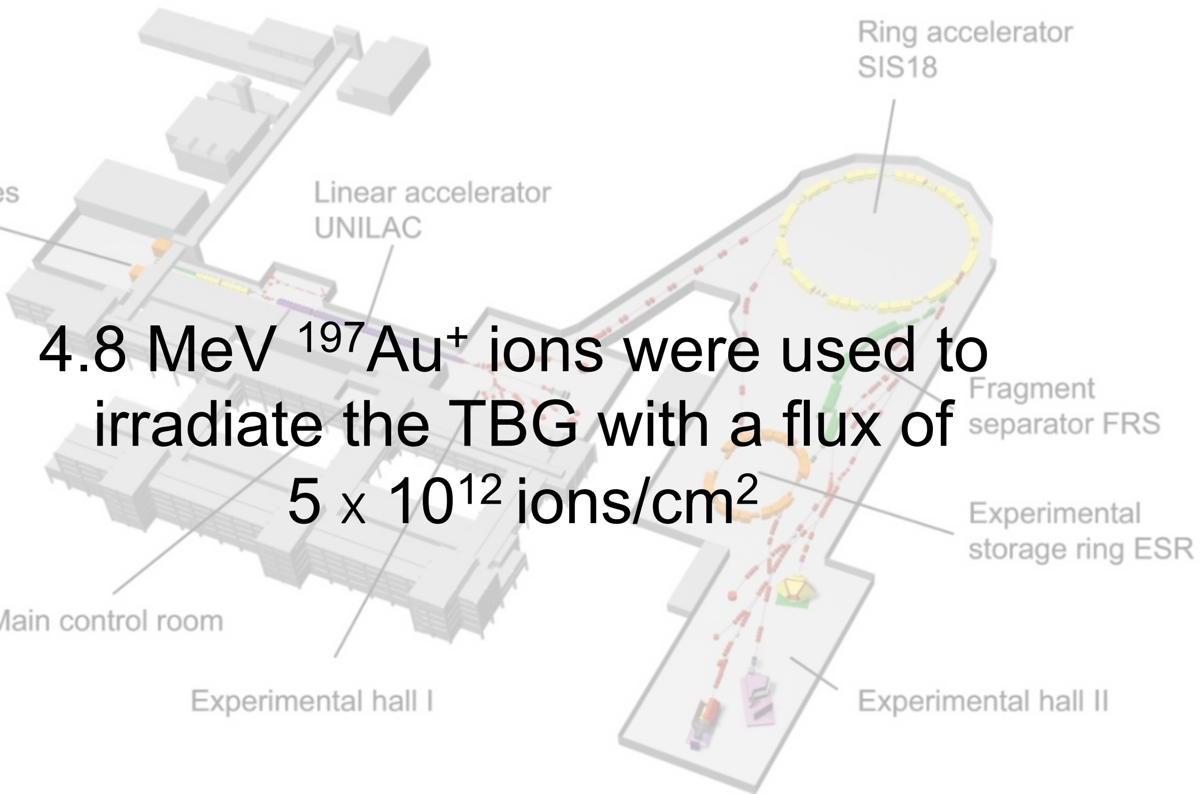
Experimental details

ss samples



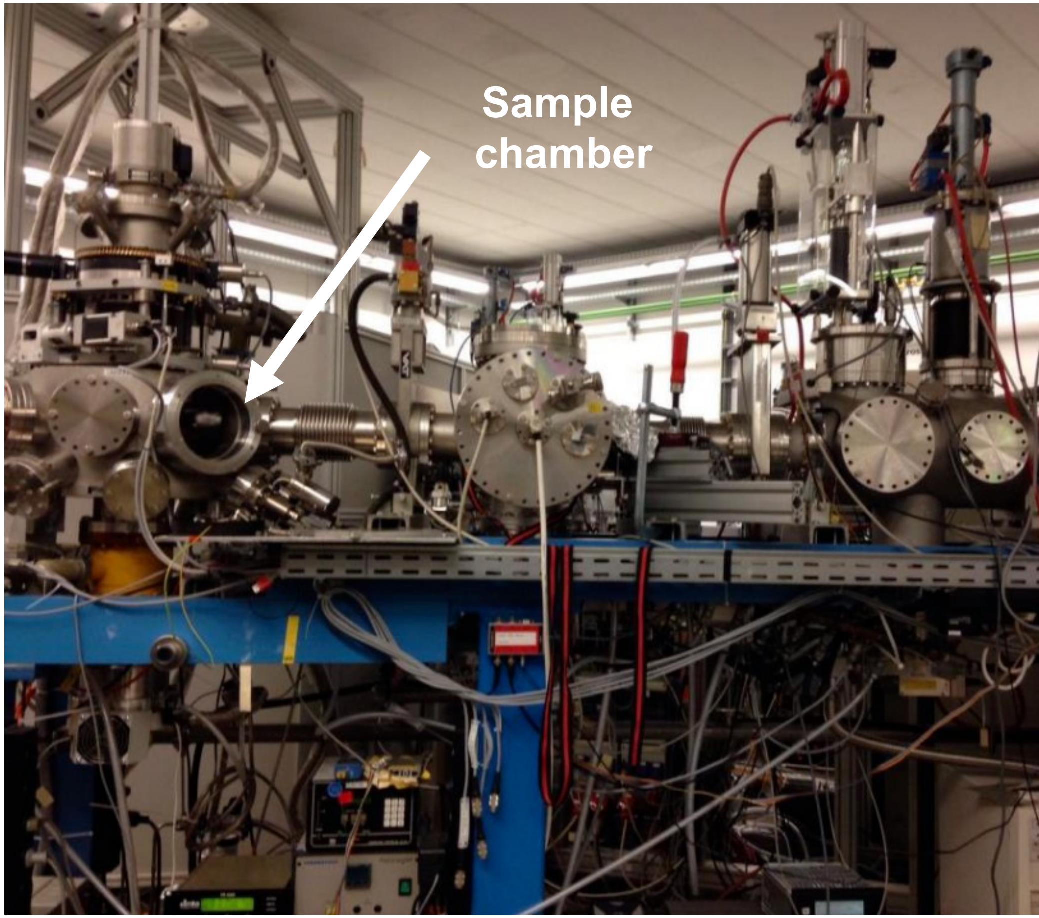
Experimental details

avy ion irradiation at the GSI Helmholtz Center in Darmstadt, Germany



4.8 MeV $^{197}Au^{+}$ ions were used to irradiate the TBG with a flux of 5×10^{12} ions/cm^2

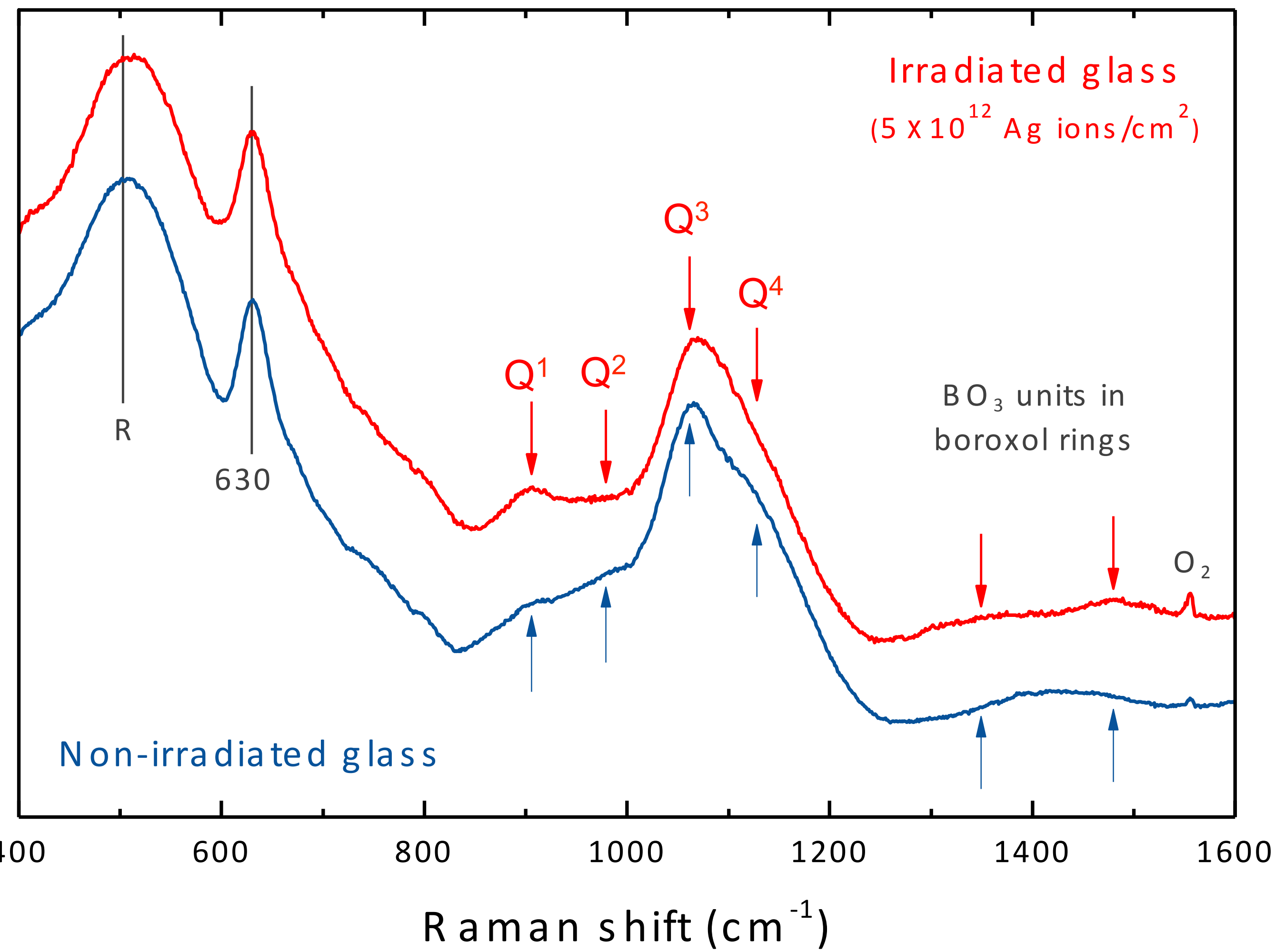
Schematic view of the accelerator in Darmstadt

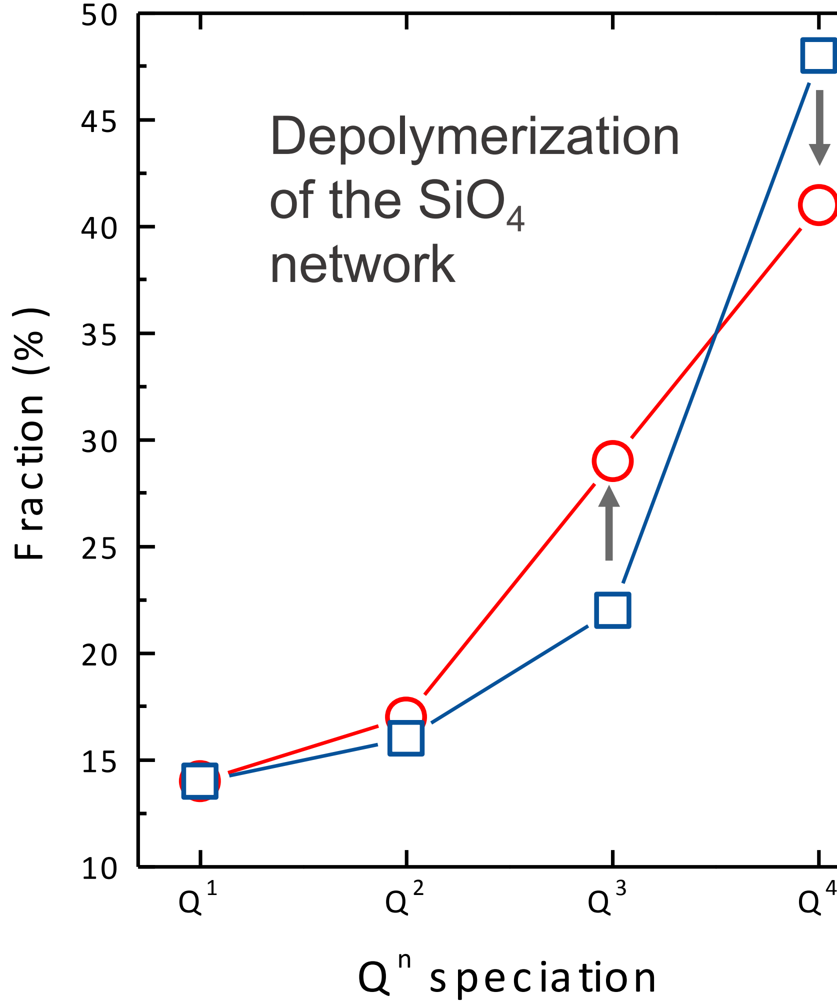


Experimental hall II

Experimental details

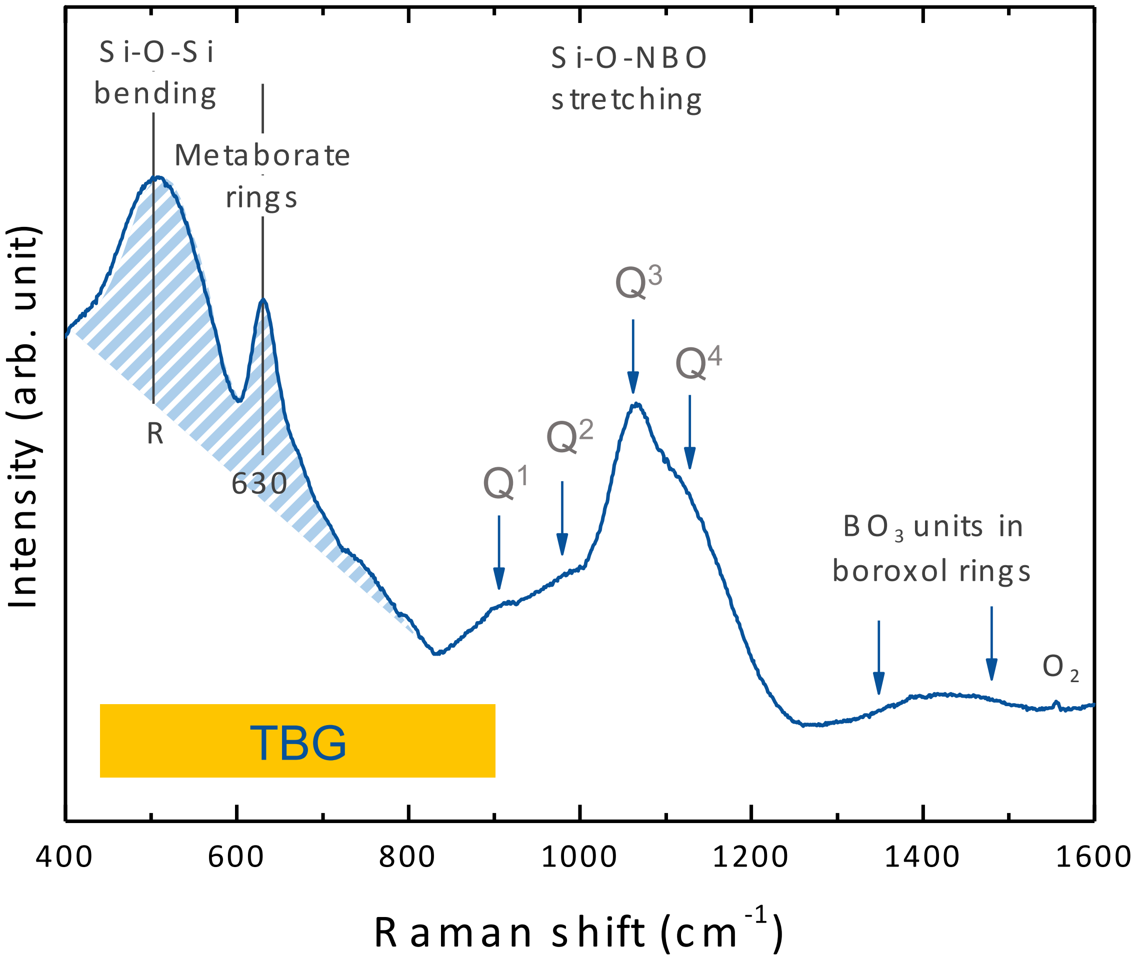
Structural effects of heavy ion irradiation (TBG)

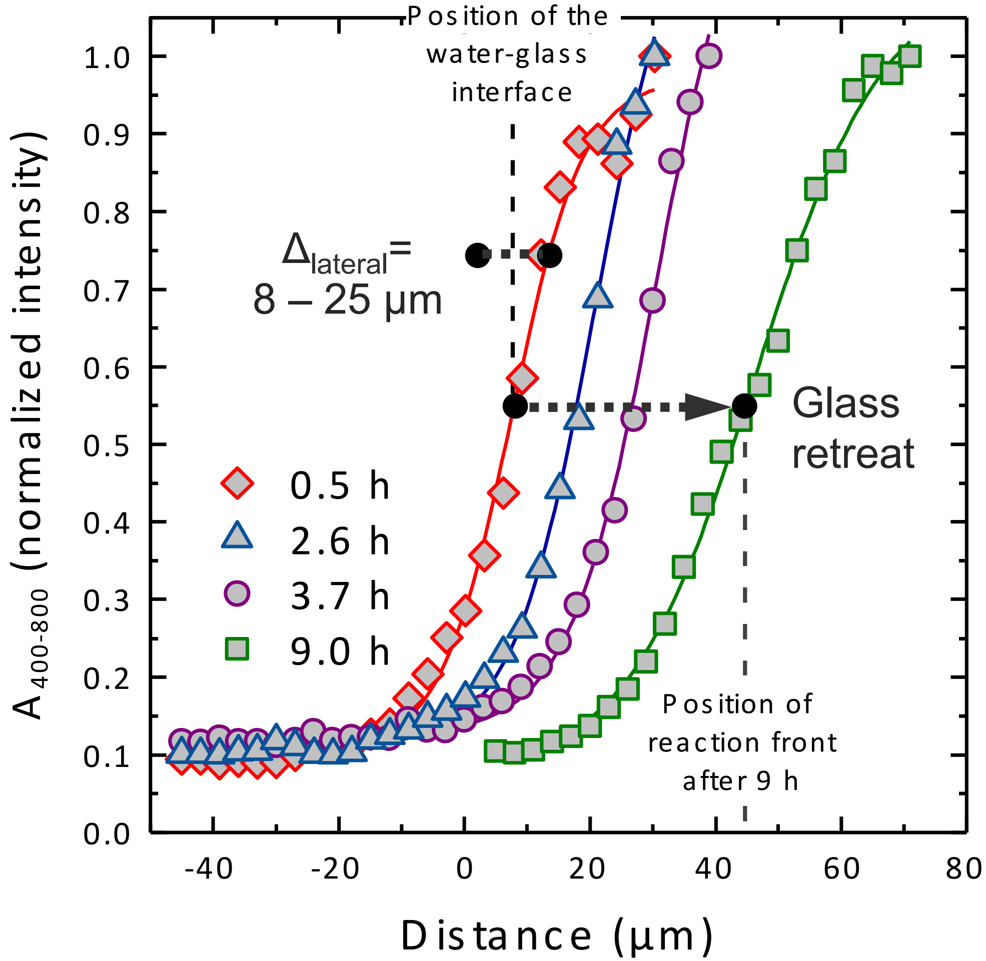




Experimental details

asuring glass retreat and spatial resolution



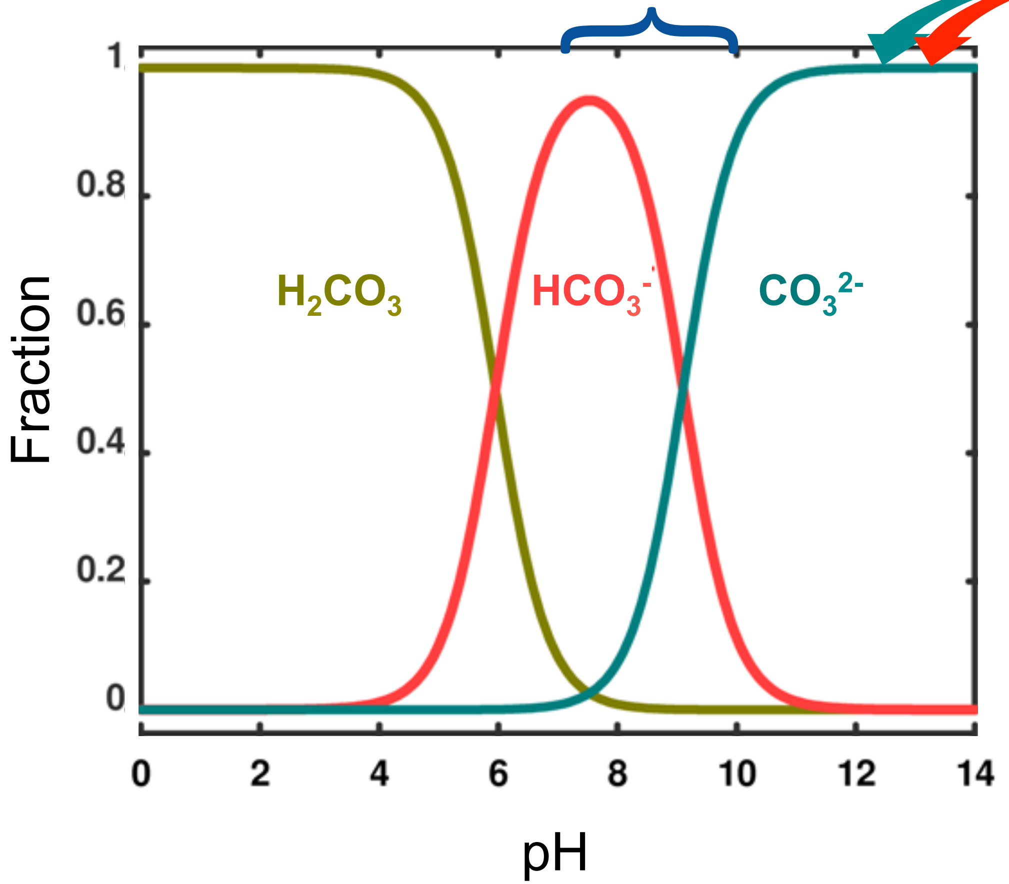


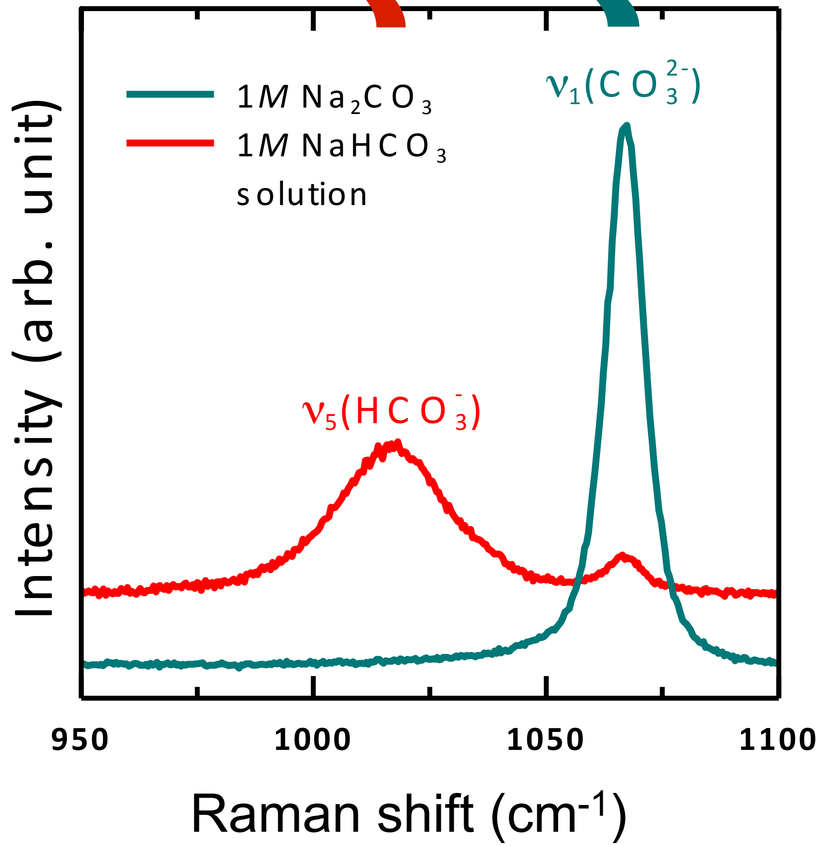
Experimental details

nitoring the solution pH at any point in space and time

he principle:

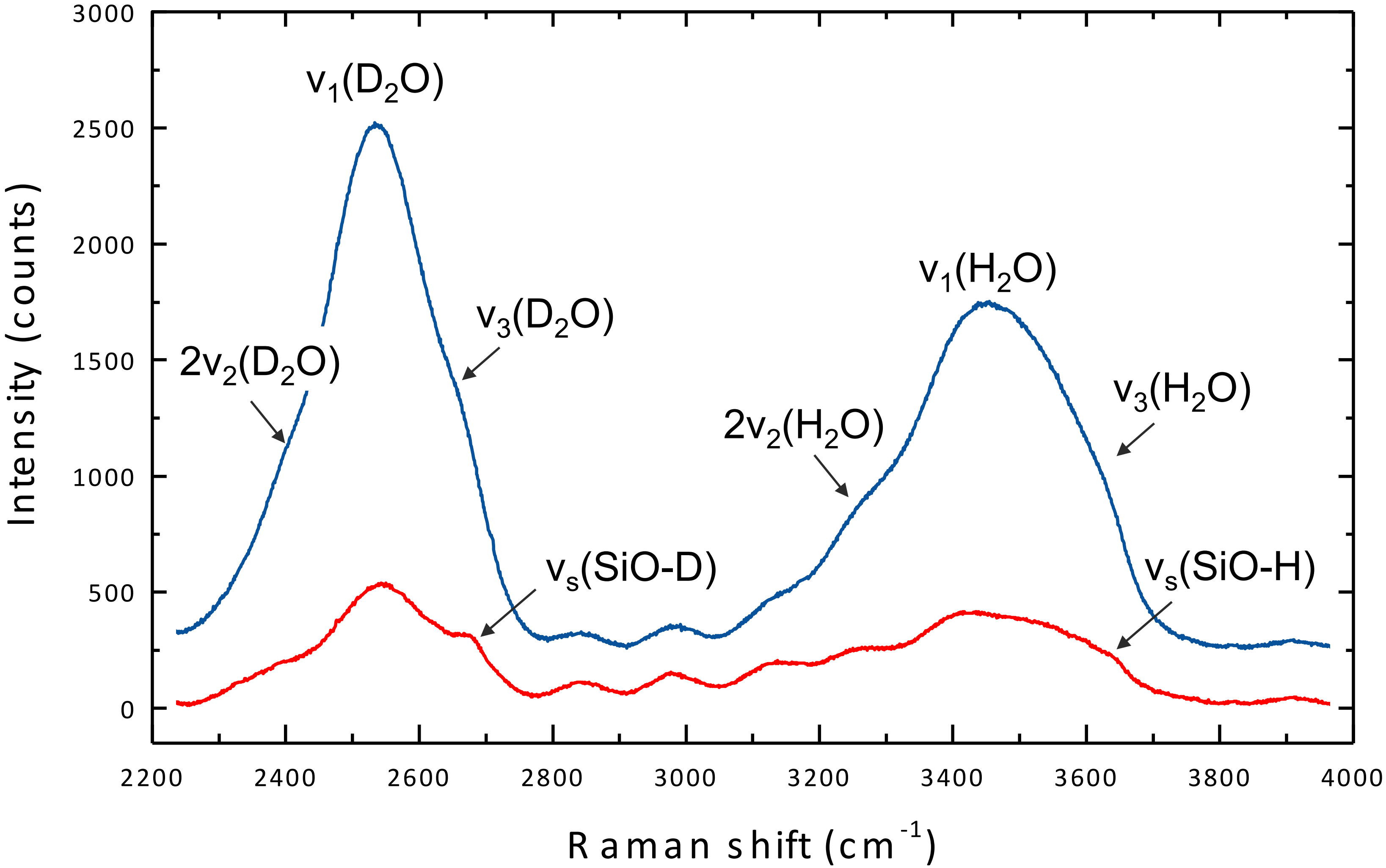
$pH = f(A_{\nu_1(CO_3^{2-})}/A_{\nu_5(HCO_3^-)})$





Experimental details

nitoring the diffusion (and reaction) of molecular water through the rim



Experimental details

eriments

Experiment #1 – TBG , 70°C, 0.1*M* HCl ($pH_{70°}$= 1.0)
→ Gap formation and silica aging

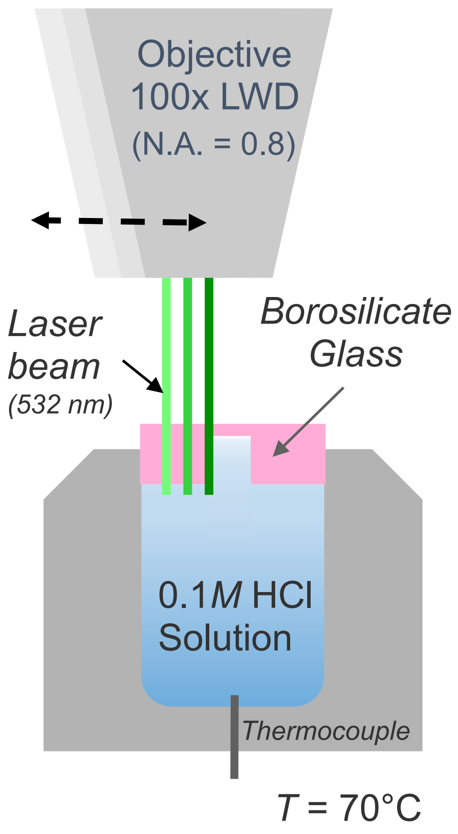
Experiment #2 - TBG, 90°C, 0.5M $NaHCO_3$ ($pH_{90°C}$ = 7.2)
→ pH gradient in a solution boundary layer

Experiment #3 - CaNaG, 90°C, 0.5*M* $NaHCO_3$ ($pH_{90°C}$ = 7.2)
→ Effect of secondary phase formation on pH

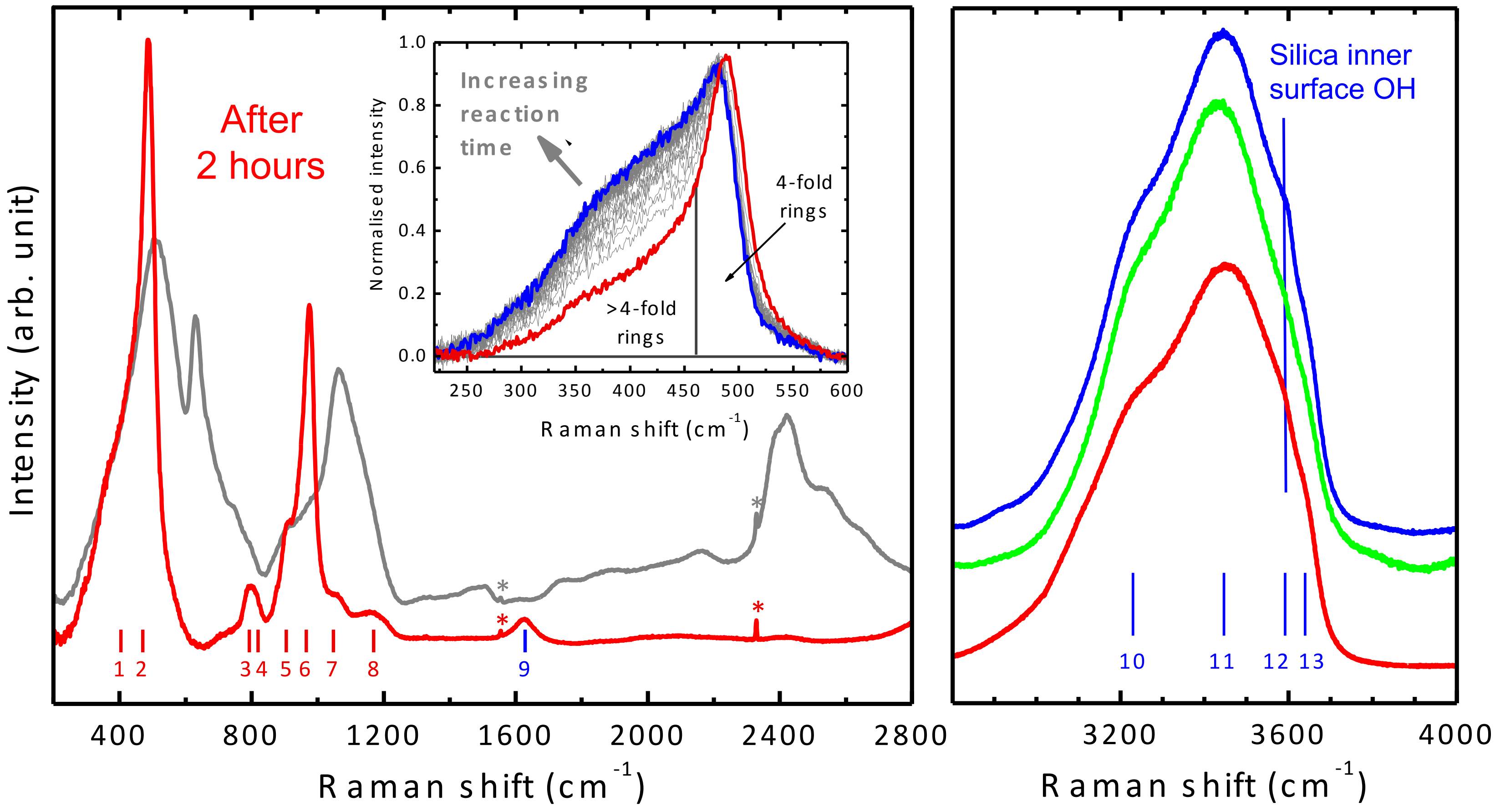
Experiment #4 – TBG, 90°C, 0.5*M* $NaHCO_3$ ($pH_{90°C}$ = 7.2), after 140 h injection of D_2O
→ pH gradient in solution and corrosion rim and diffusion of water through the rim

Experiment(s) #5 – TBG und $TBG_{irradiated}$, 90°C, 0.5M $NaHCO_3$ ($pH_{90°C}$ = 7.2)
→ Effect of heavy ion irradiation on the forward dissolution rate (r_0)

periment #1 - Gap formation and silica aging

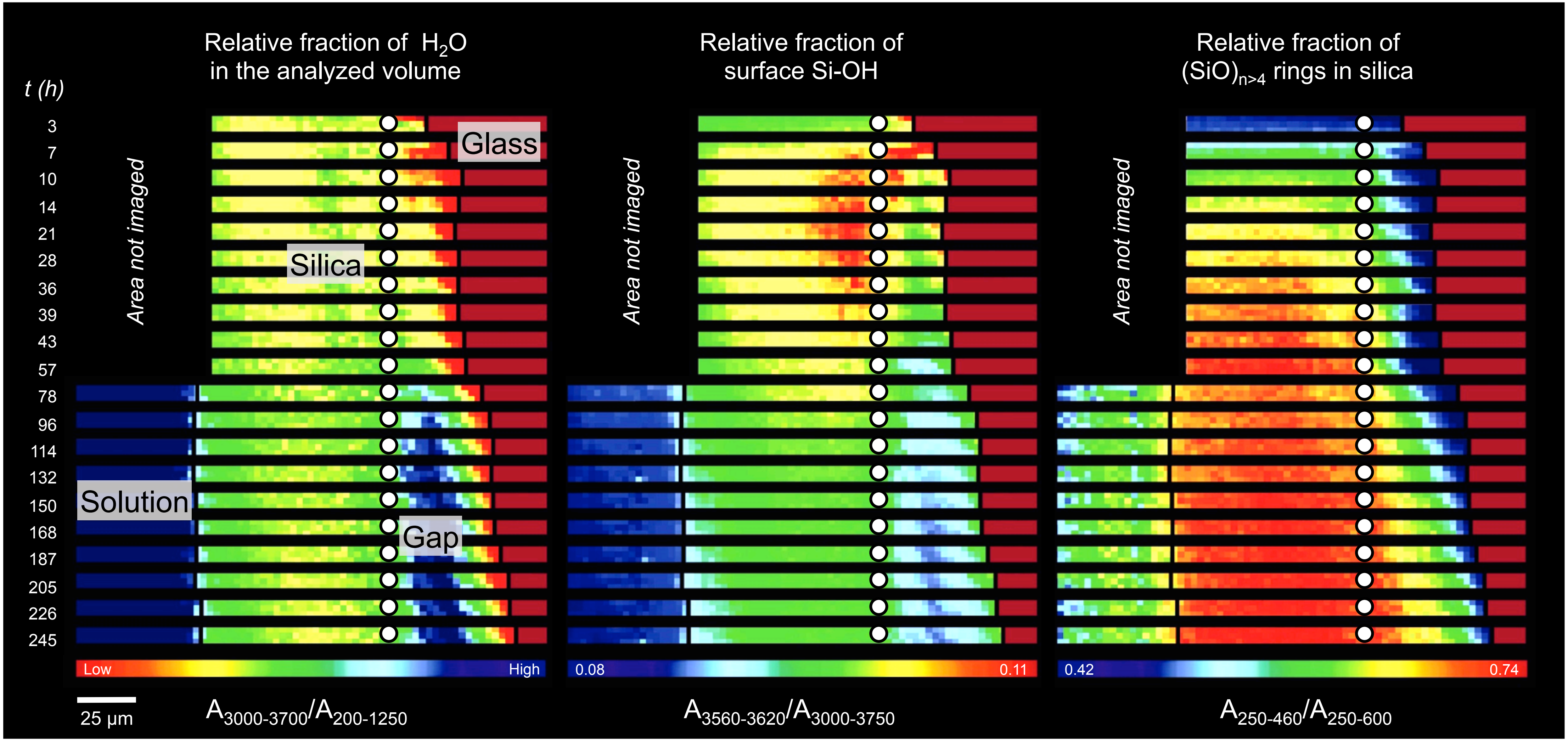


Experimental setup



Results of in-situ experiments

periment #1: Gap formation and silica aging



Results of in-situ experiments

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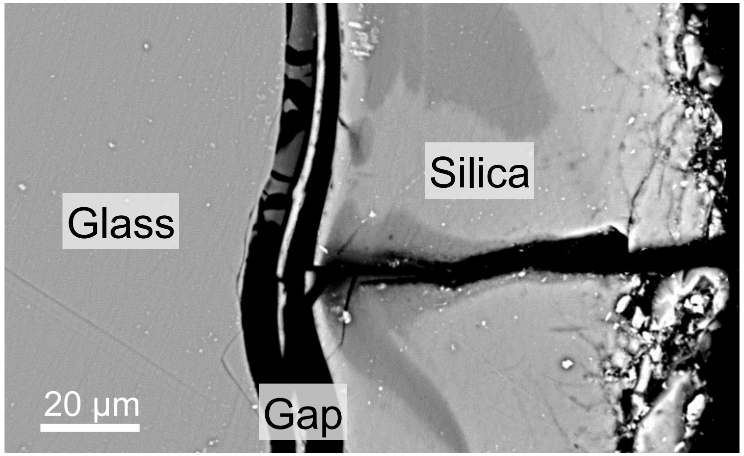
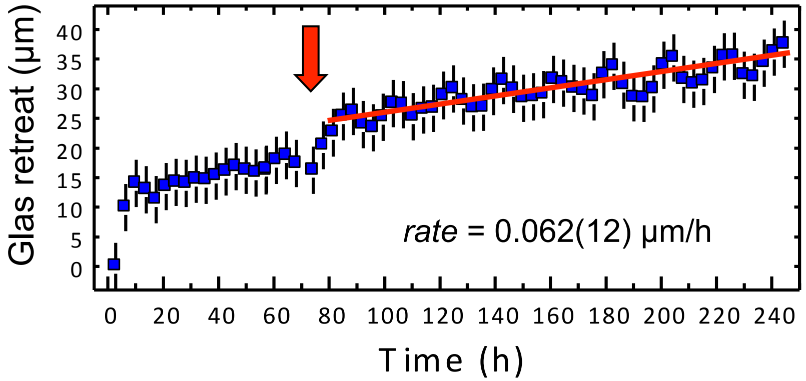
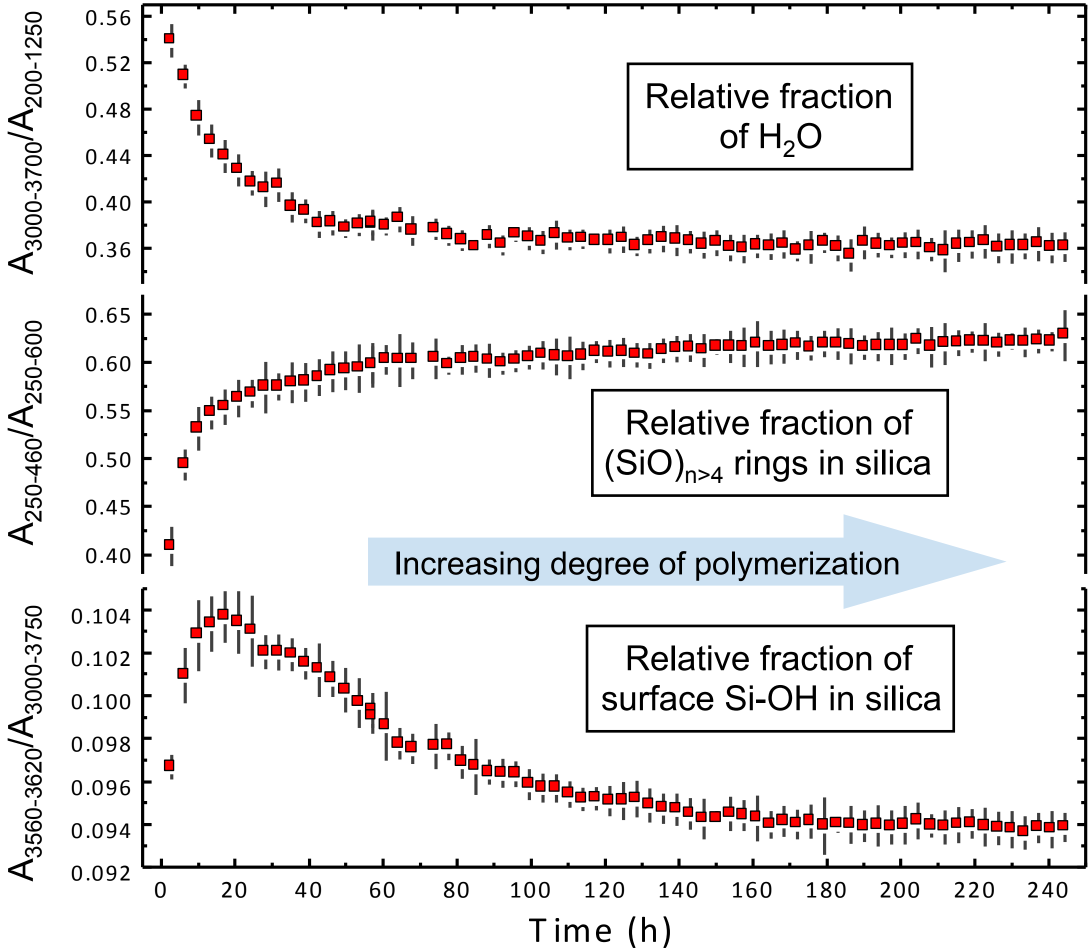


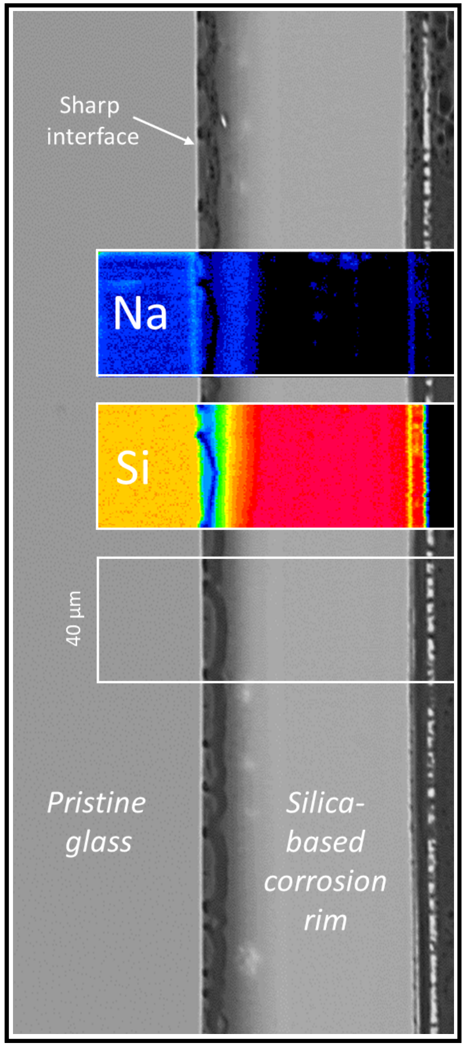
BSE image of altered glass after the experiment

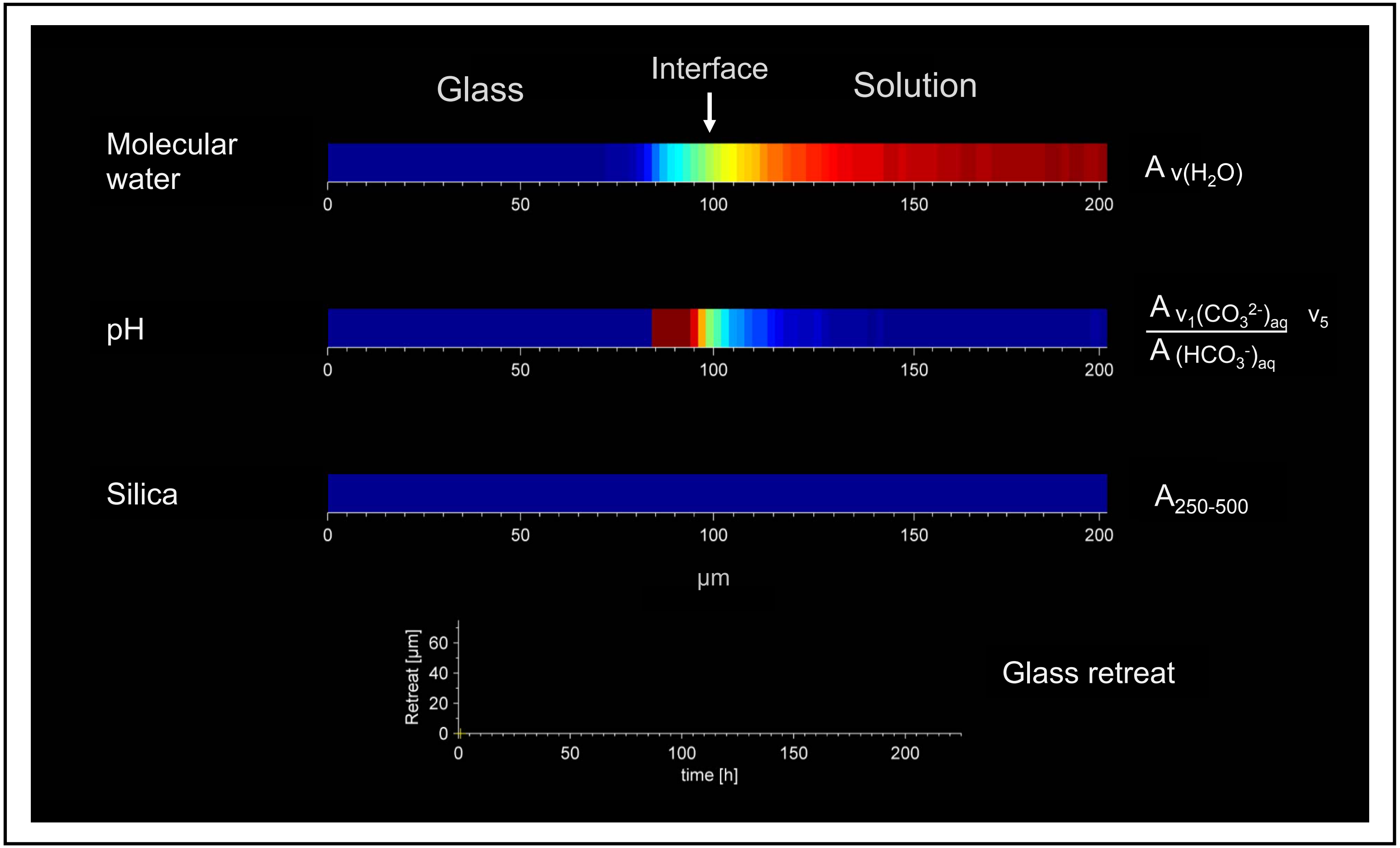




Results of in-situ experiments

…periment #2 - pH gradient in a solution boundary layer





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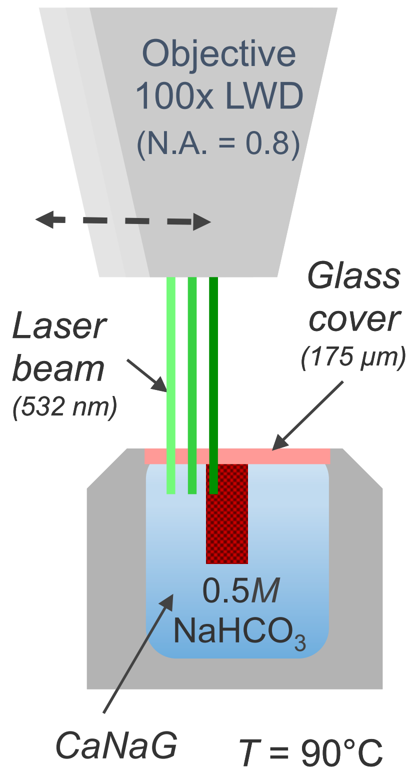
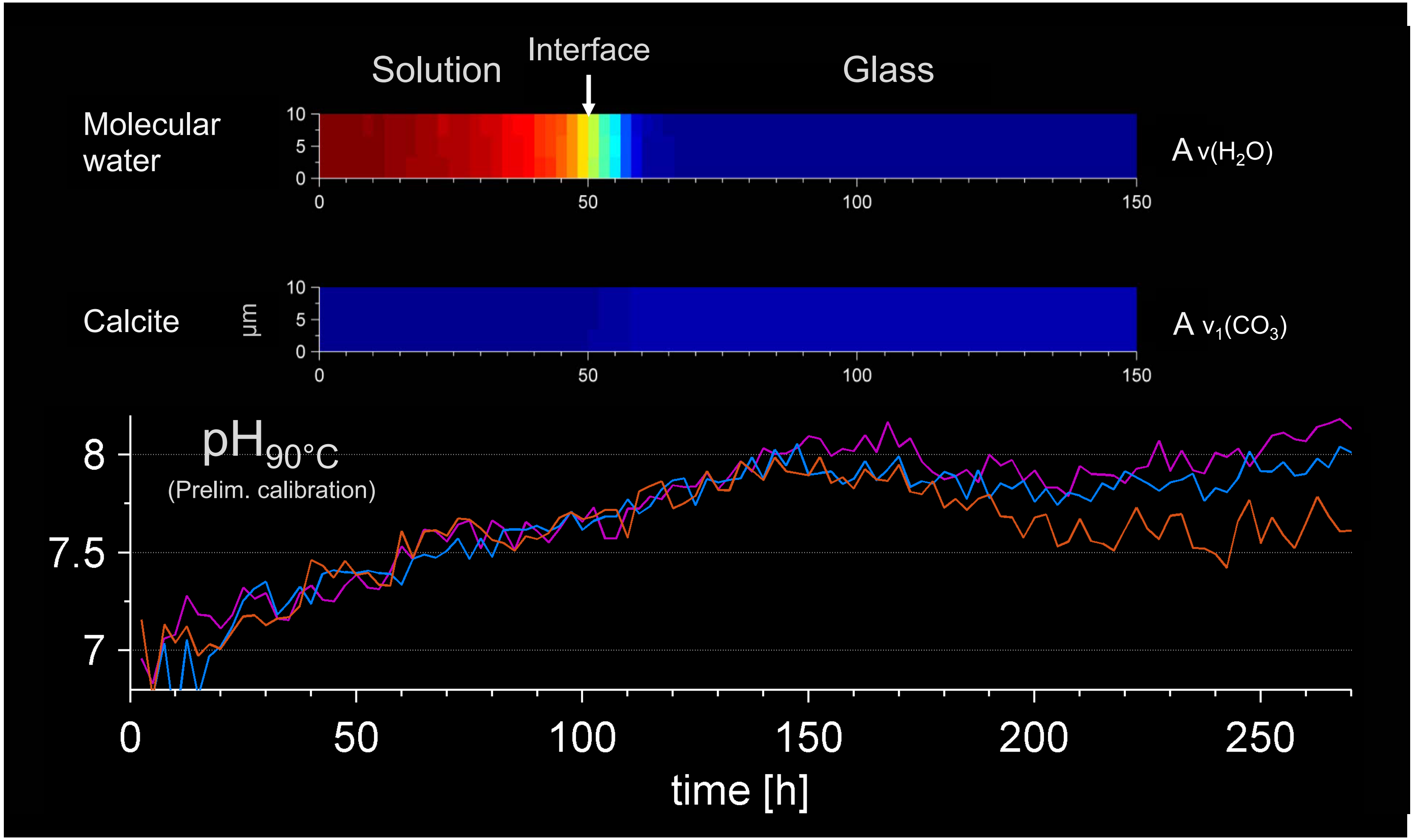
periment #3 - Effect of secondary phase formation on pH



Experimental setup



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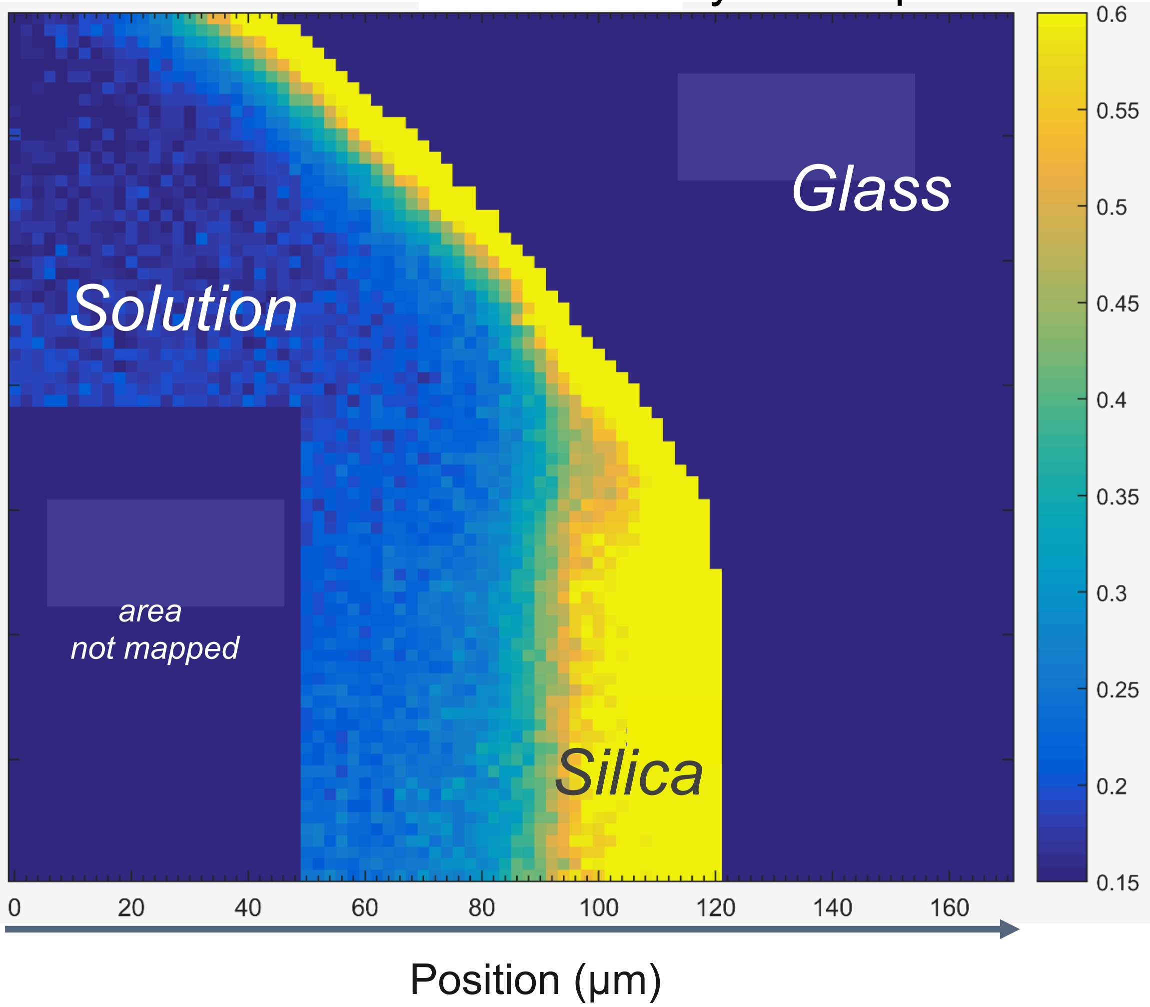
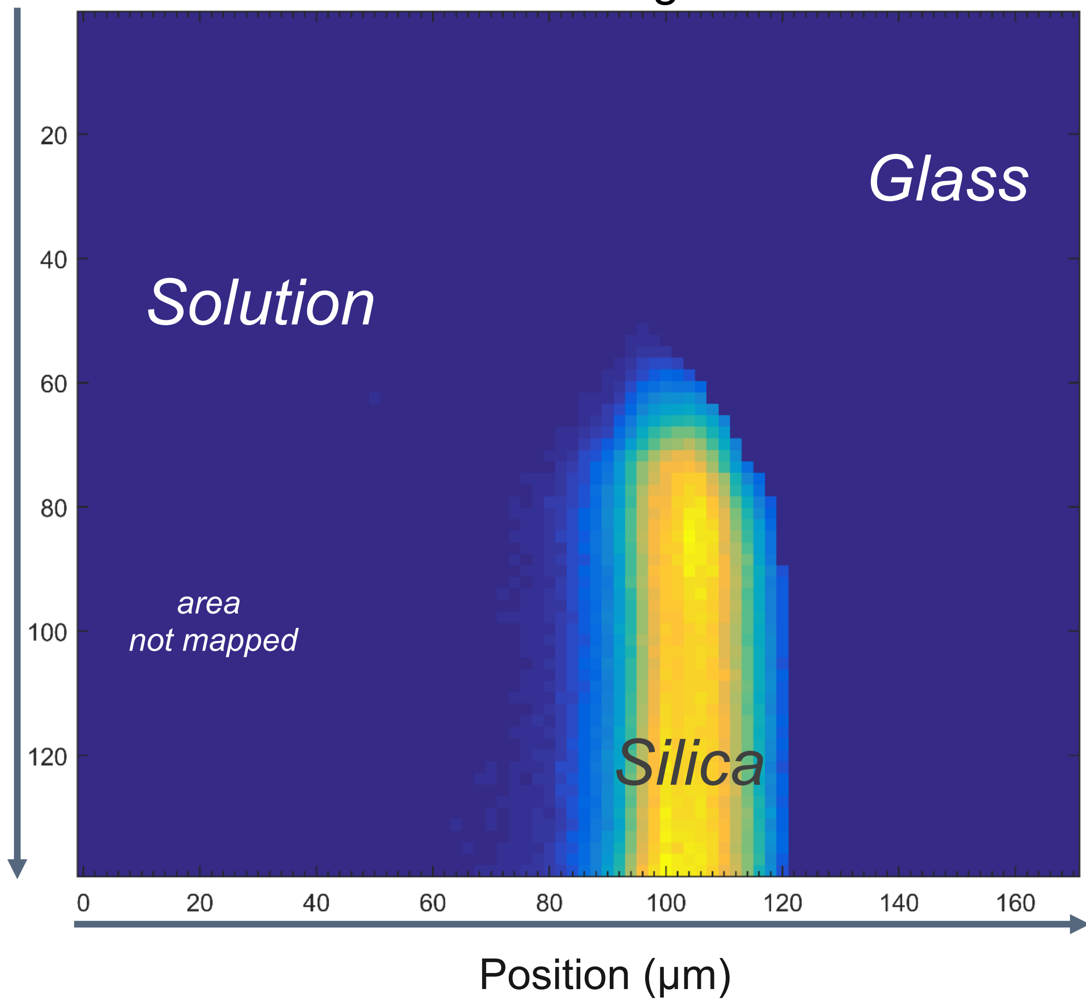
Results of in-situ experiments

periment #4 – pH gradient in solution and the corrosion rim

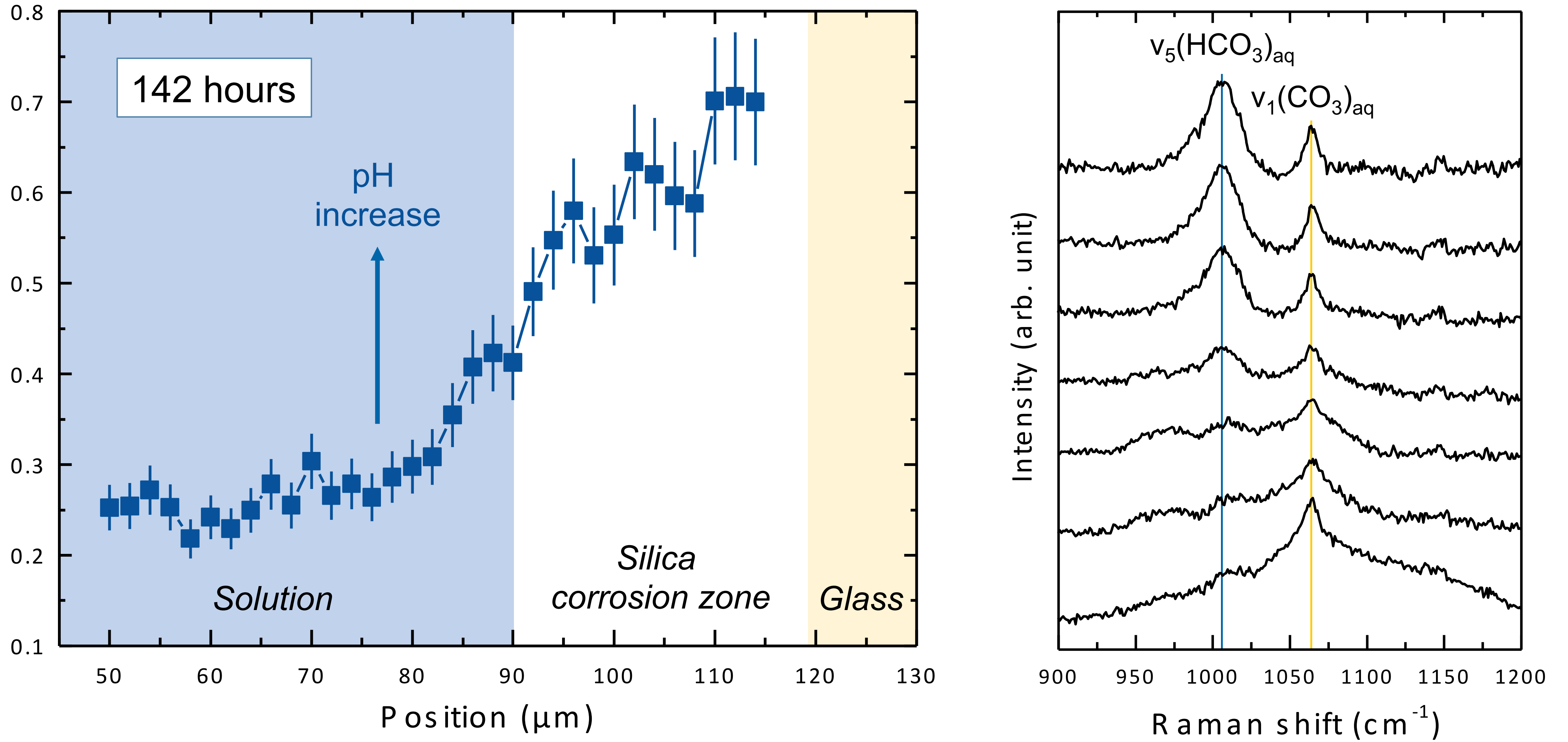
Carbonate-bicarbonate intensity ratio ~ pH



Silica Si-O-Si breathing mode intensities

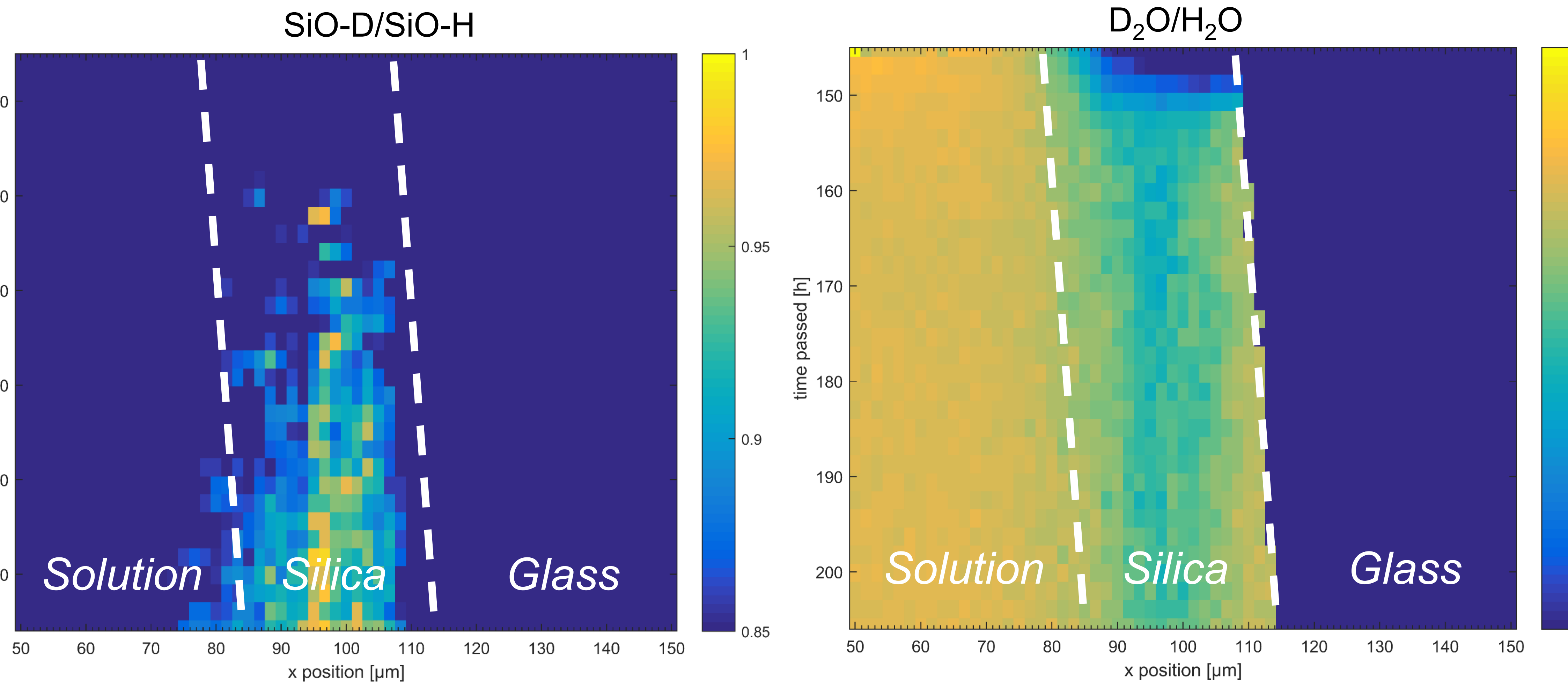


eriment #4 – pH gradient in solution and the corrosion rim



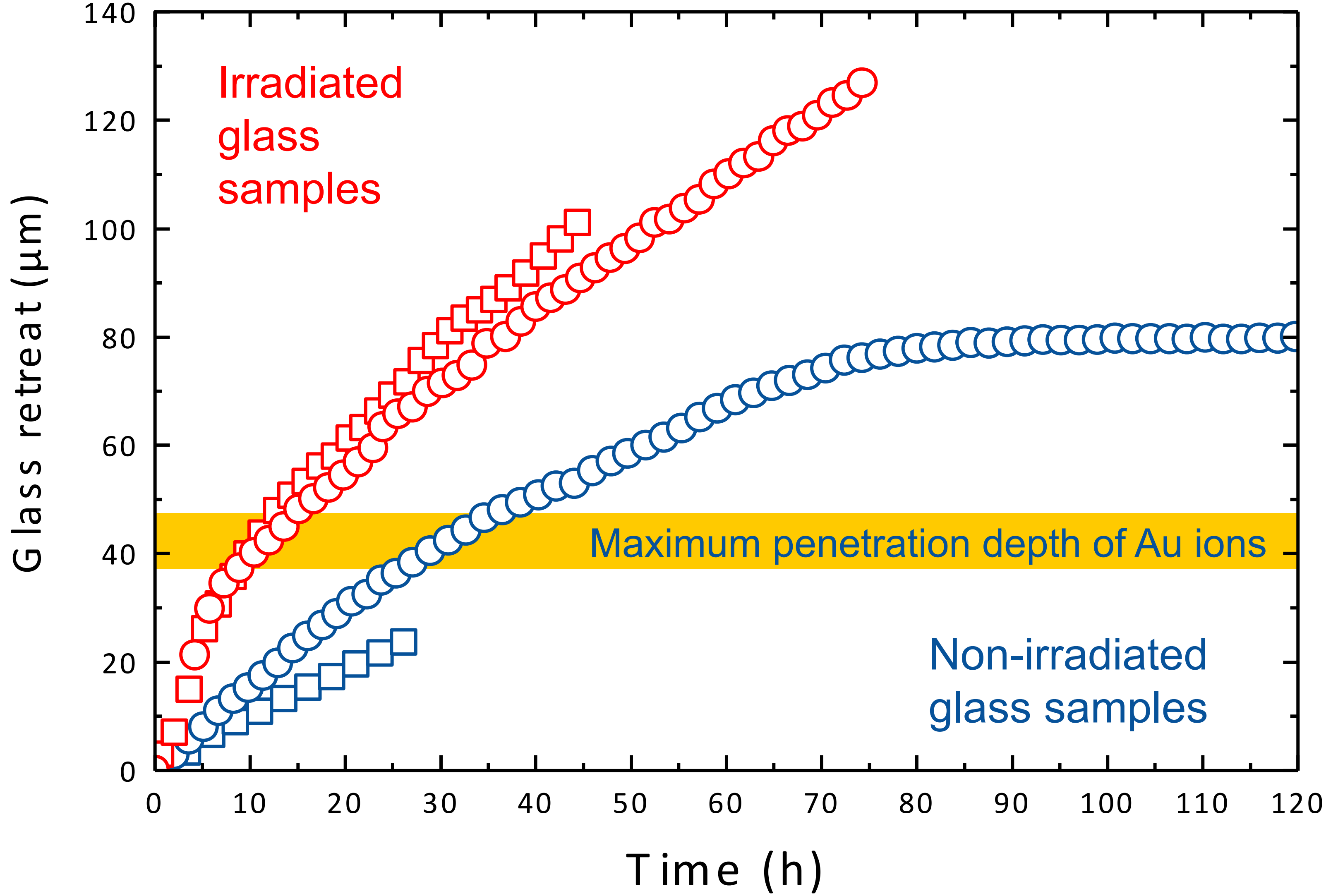
Results of in-situ experiments

periment #4 – Diffusion and reaction of molecular water within the corrosion rim



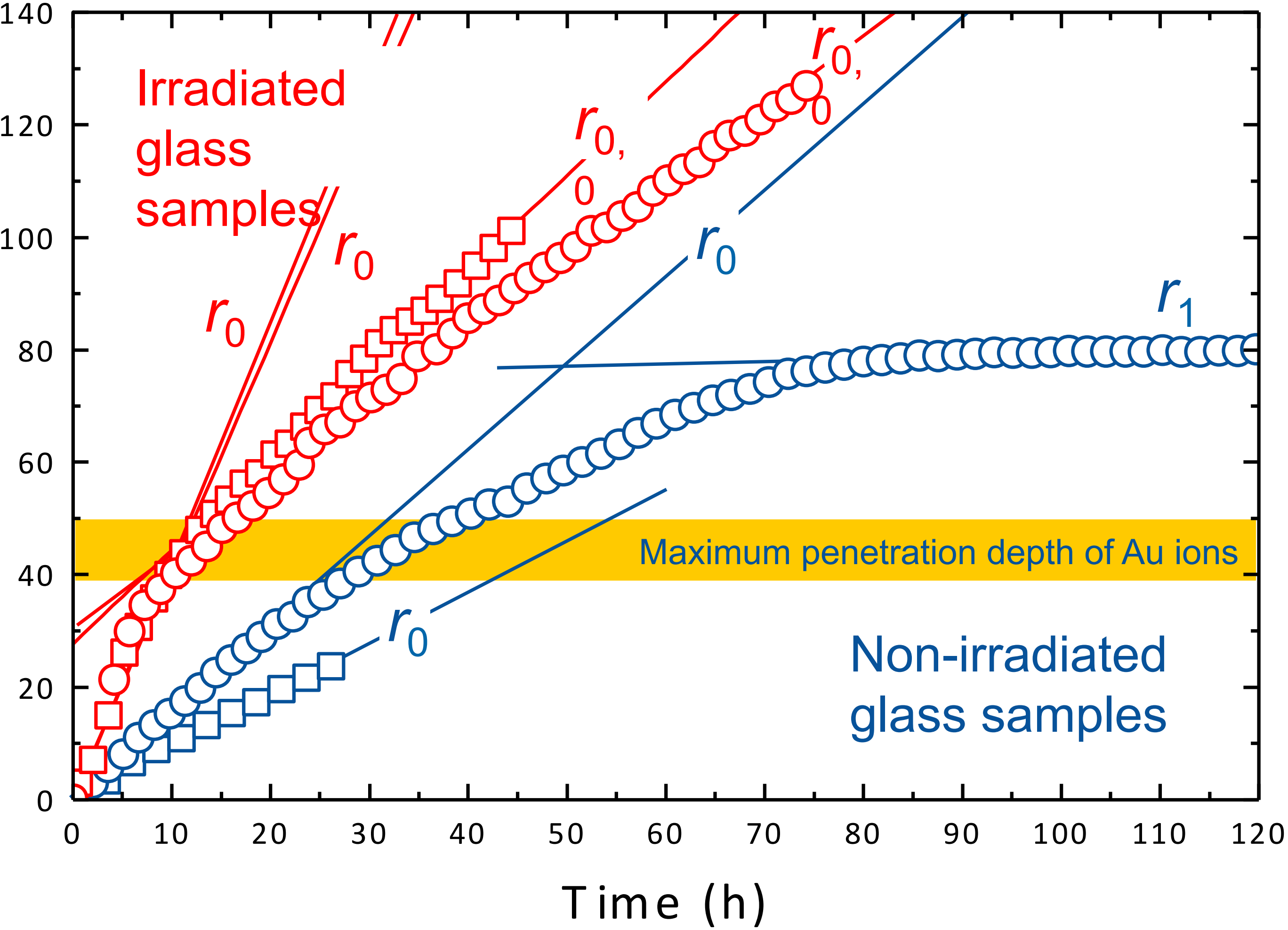
Results of in-situ experiments

periment #5 - Effect of heavy ion irradiation on the forward dissolution rate (r_0)



Results of in-situ experiments

...periment #5 - Effect of heavy ion irradiation on the forward dissolution rate (r_0)



Exp.	r_0	$r_{0,0}$	r_1
	(µm/h)		
#5-1	1.532 (± 0.015)	-	0.01 (± 0.00
#5-2	0.936 (± 0.022)	-	-
#5-3	4.62 (± 0.39)	1.339 (± 0.027)	-
#5-4	4.35 (± 0.24)	1.666 (± 0.056)	-

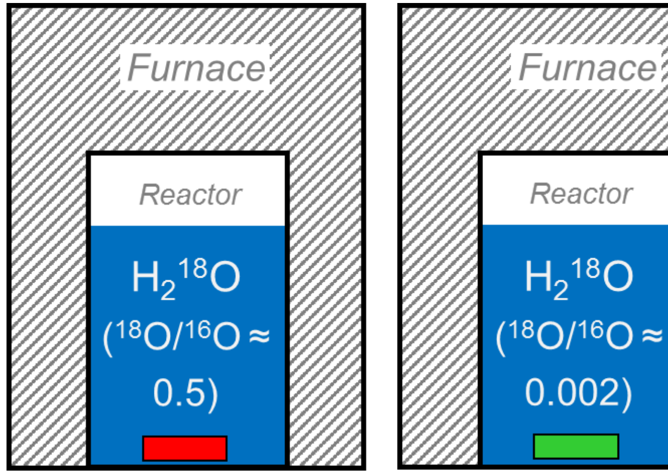
Errors represent 2-sigma errors of the lin

Experimental details

periments

Experimental series #1

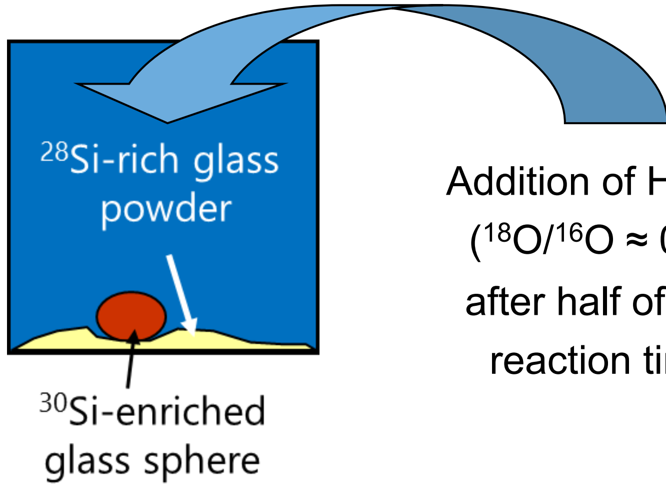
- TBG monoliths
- pure H_2O
- 90°C
- multiple sample exchange between ^{18}O-labelled and -unlabelled solution



Glass samples were exchanged five ti

Experimental series #2

- TBG powder and TBG spheres enriched with ^{30}Si
- different initial pH adjusted with HCl and KOH
- 90°C
- addition of ^{18}O after half of the total reaction time

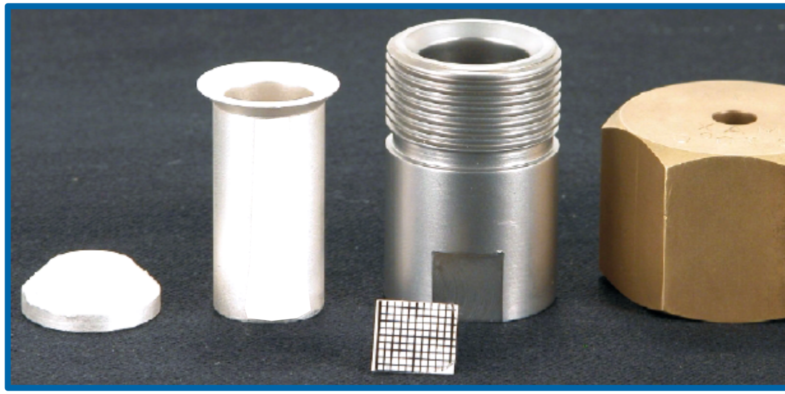


Experimental details

periments

xperimental series #3

- ISG and QBG monoliths
- pre-altered at 90°C for 9 months
- then altered at 90°C (ISG) and 150°C (QBG) for 3 months in multi-isotope tracer solutions*
- pH = 7.0 (continuously re-adjusted)



sotope solution tracers

$\mathbf{D}_2O$ (D/H = 0.23), $H_2{}^{\mathbf{18}}\mathbf{O}$ ($^{18/16}O$ = 0.23), $^{\mathbf{10}}\mathbf{B}_2O_3$ (250 ppm), $^{\mathbf{30}}\mathbf{Si}O_2$ (362 ppm), $^{\mathbf{44}}\mathbf{Ca}Cl_2$ (88 ppm

ther tracers

K (from solution preparation and pH adjustments), **F** (from PTFE)

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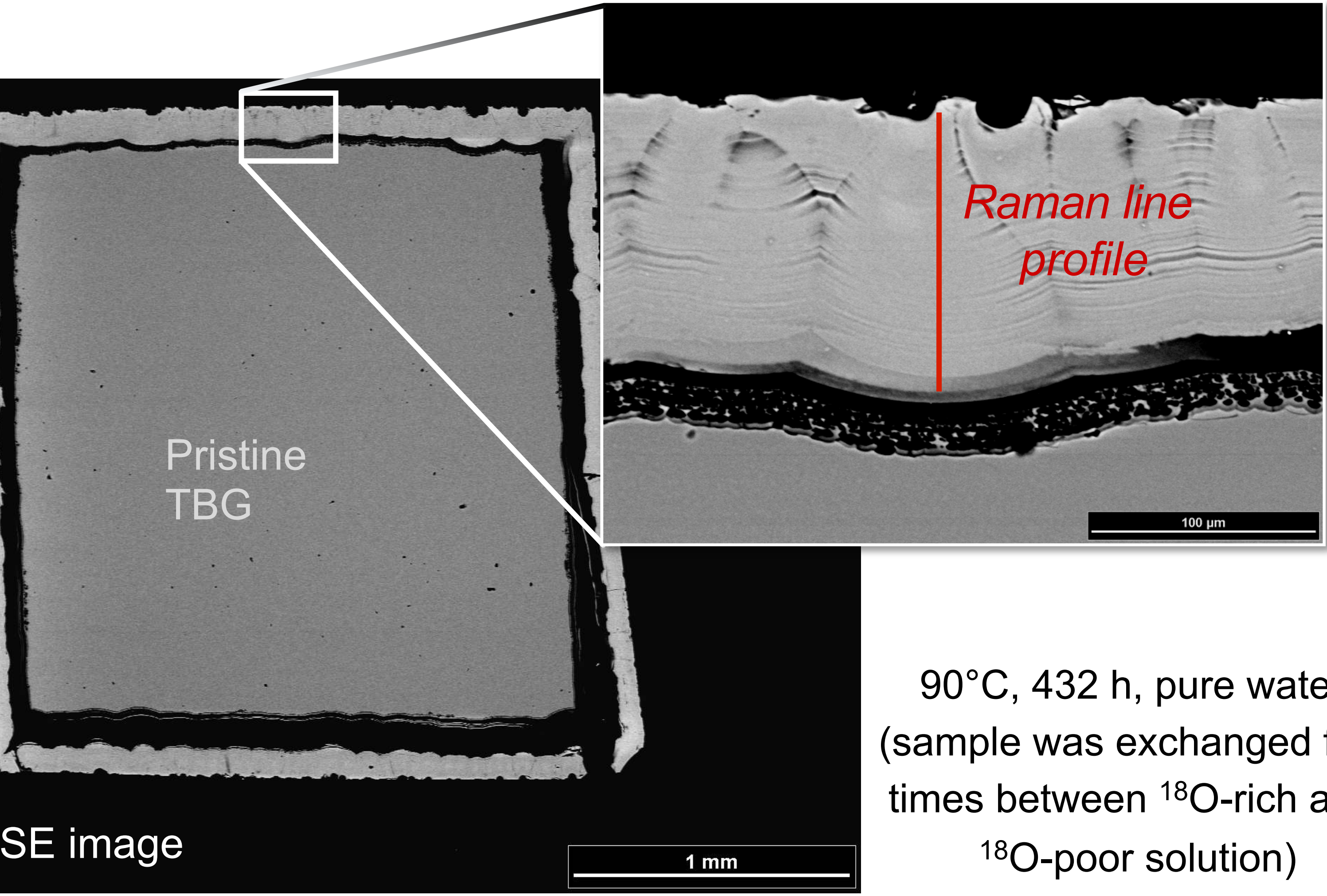
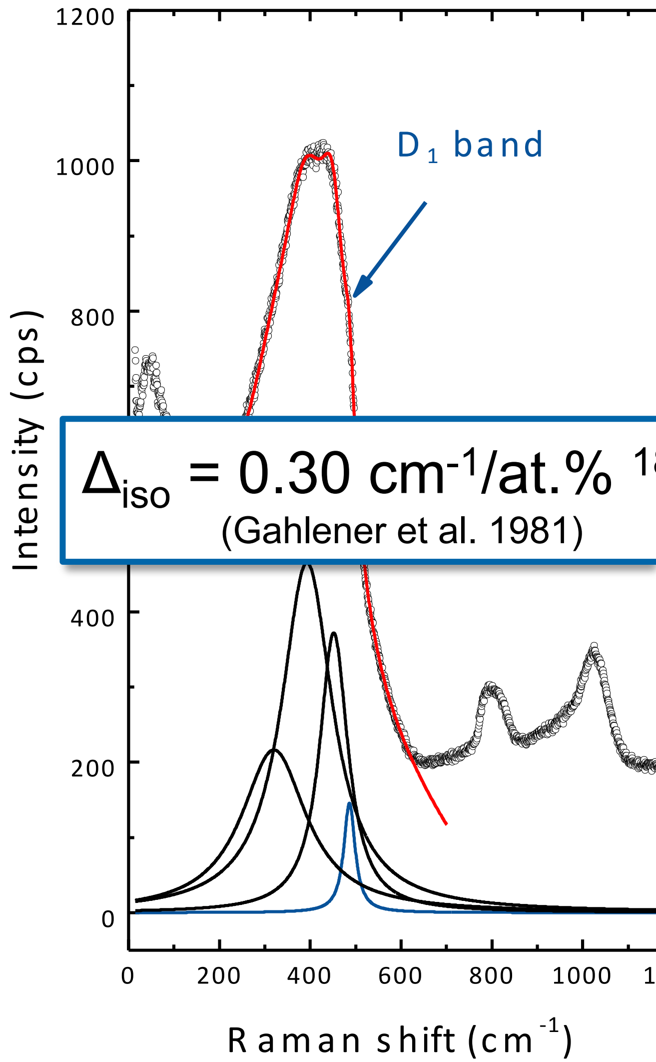
Results of isotope exchange experiments

periment #1



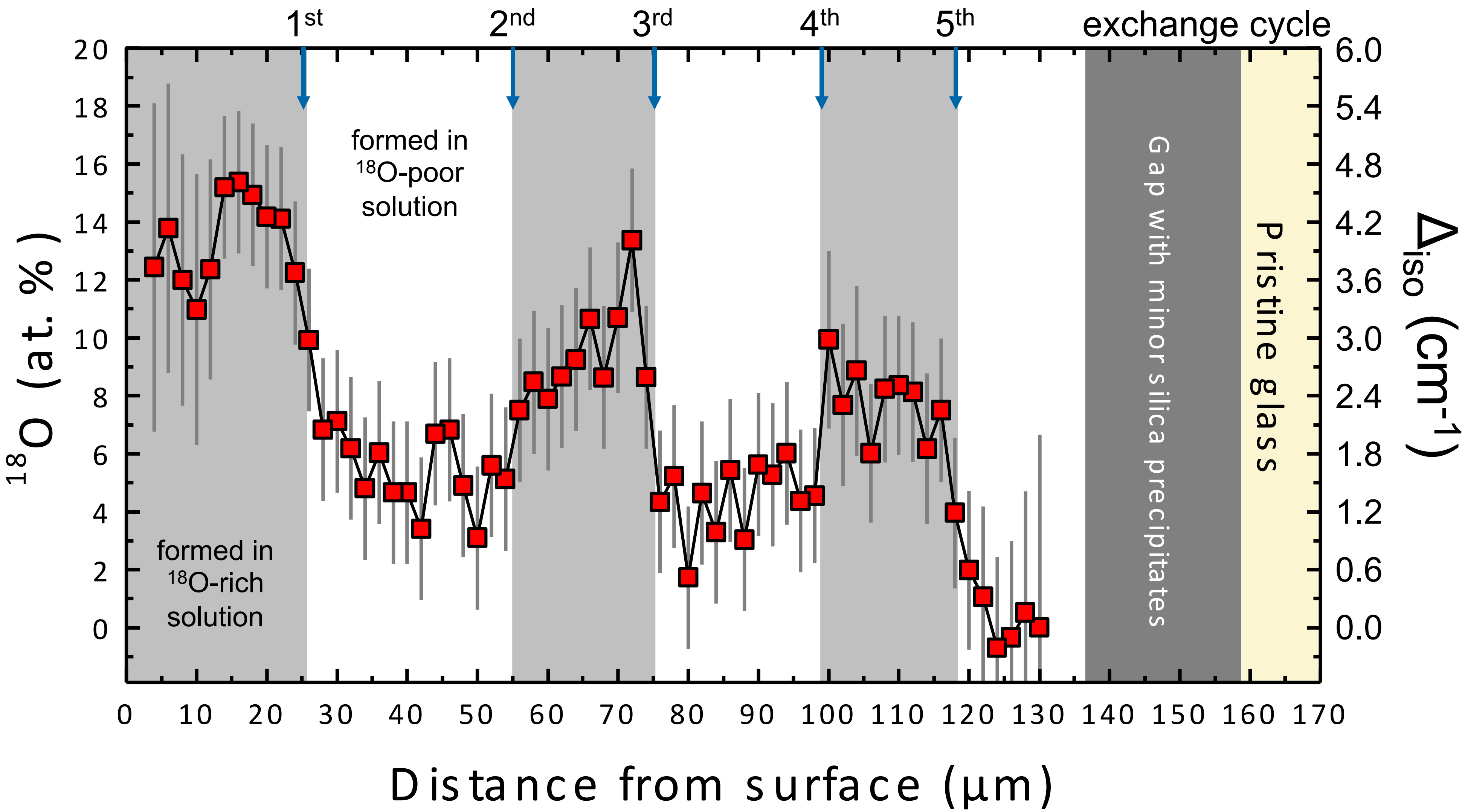
90°C, 432 h, pure water (sample was exchanged five times between ^{18}O-rich and ^{18}O-poor solution)



Δ_{iso} = 0.30 cm^{-1}/at.% 1
(Gahlener et al. 1981)

Results of isotope exchange experiments

periment #1 - Multiple oxygen isotope exchange



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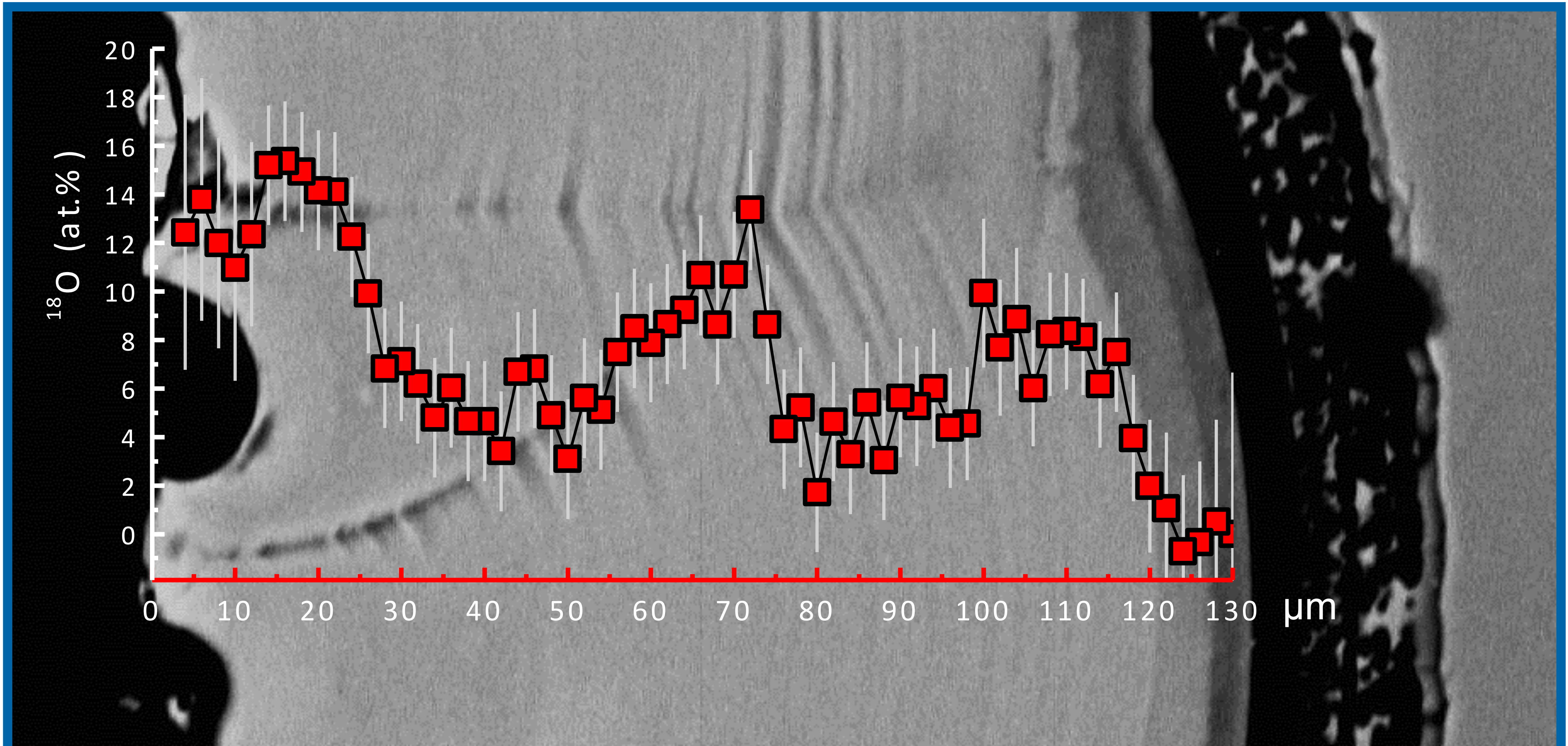
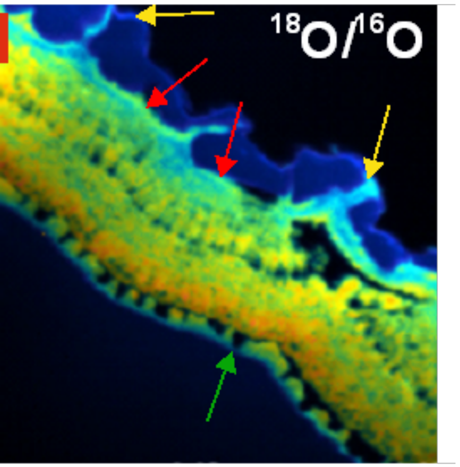
Results of isotope exchange experiments

…periment #1 - Multiple oxygen isotope exchange



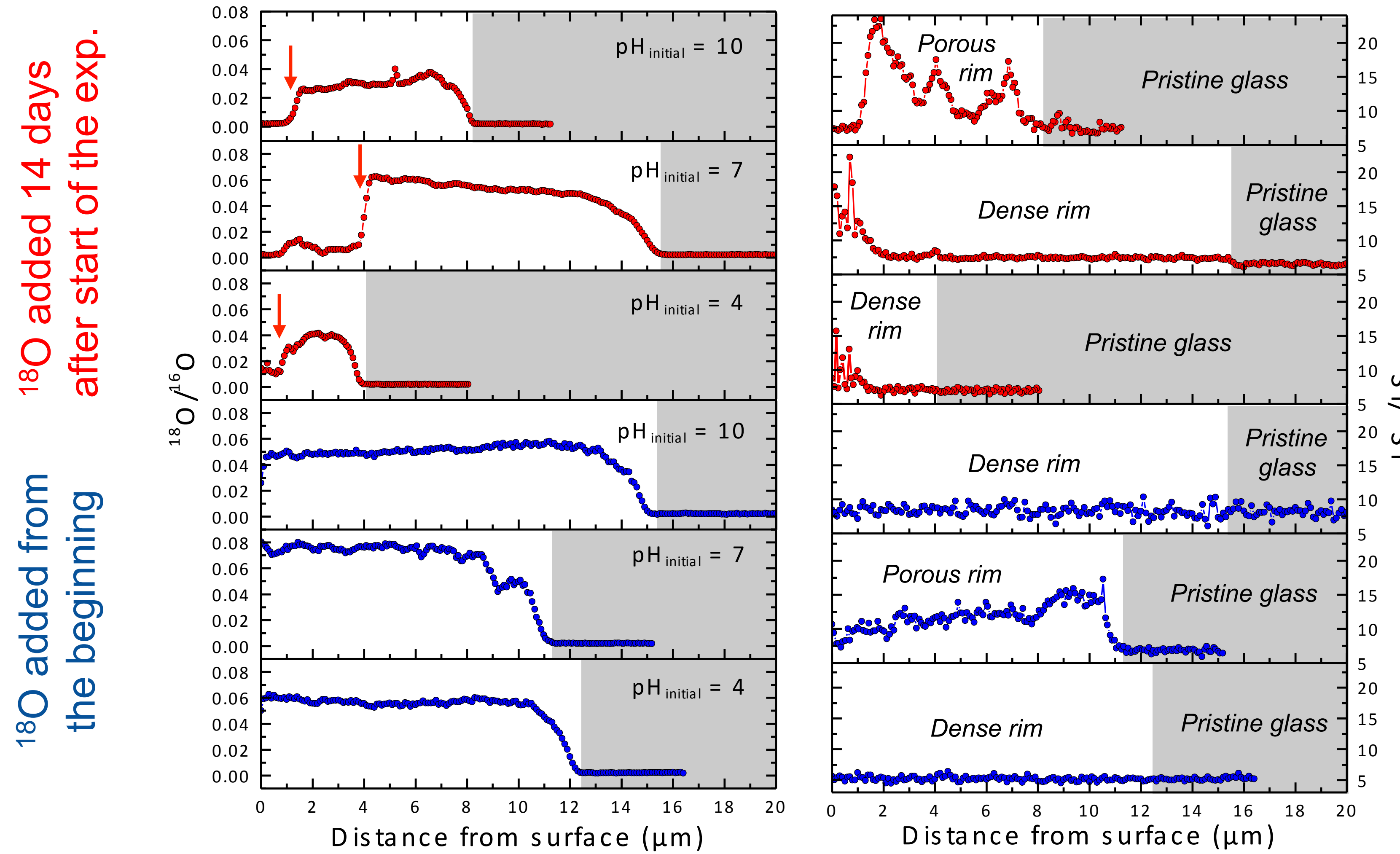
Results of isotope exchange experiments

periment #2 – Si and O isotope exchange



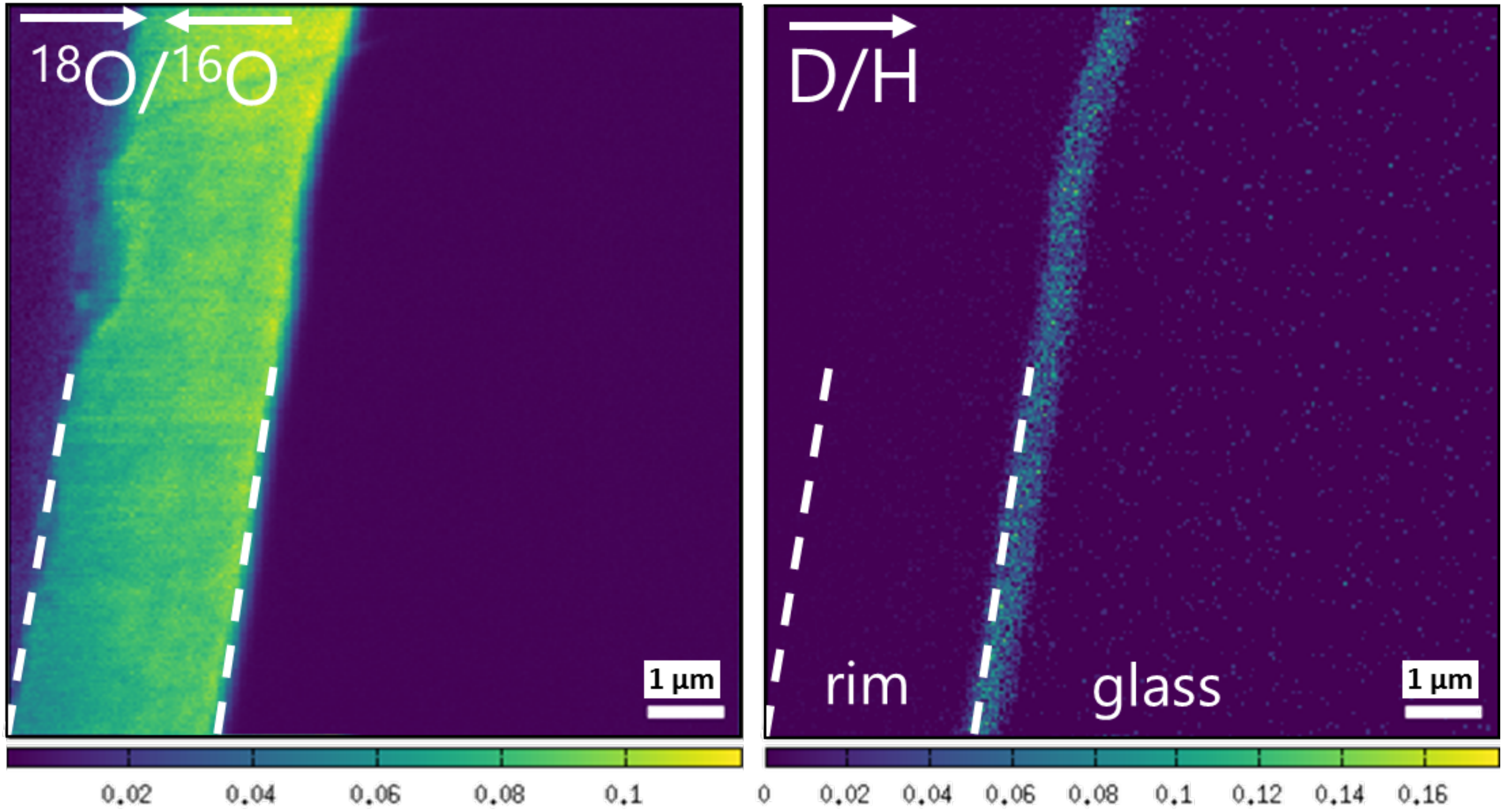
TBG: 90°C, 672 h

sler *et al.* (2015, GCA)

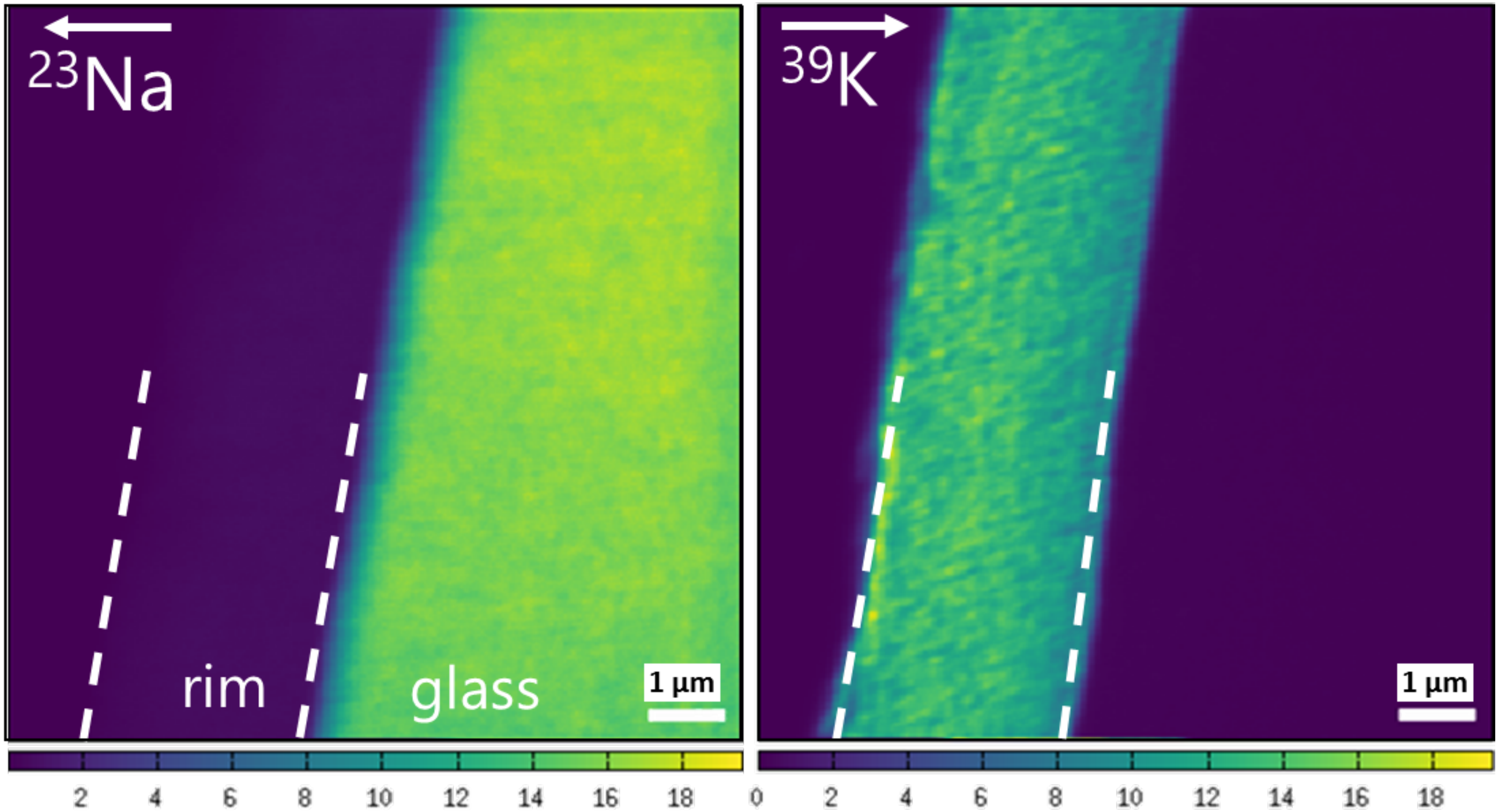


Results of isotope exchange experiments

perimental series #3: ISG, pre-altered at 90°C/90°C



perimental series #3: ISG, pre-altered at 90°C/90°C



Results of isotope exchange experiments

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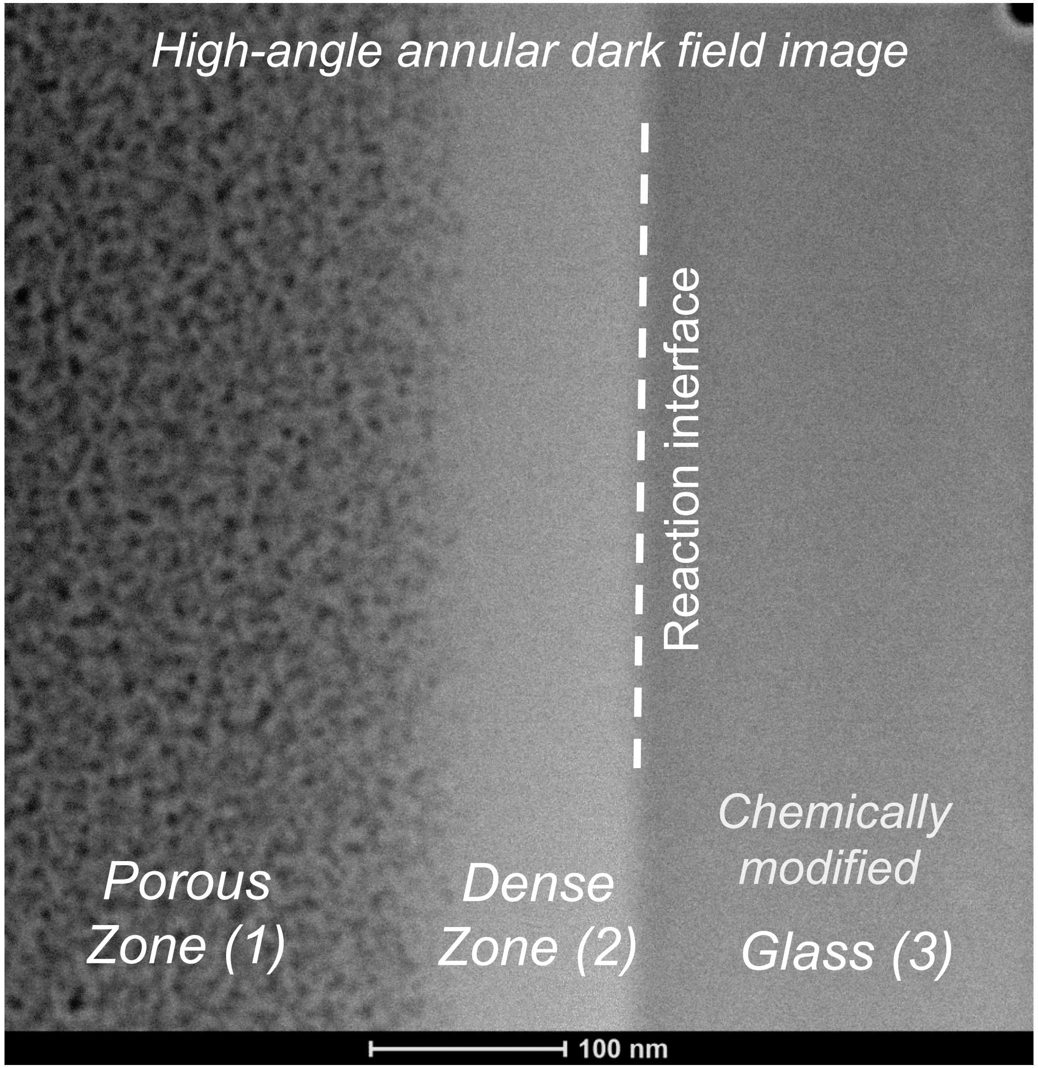
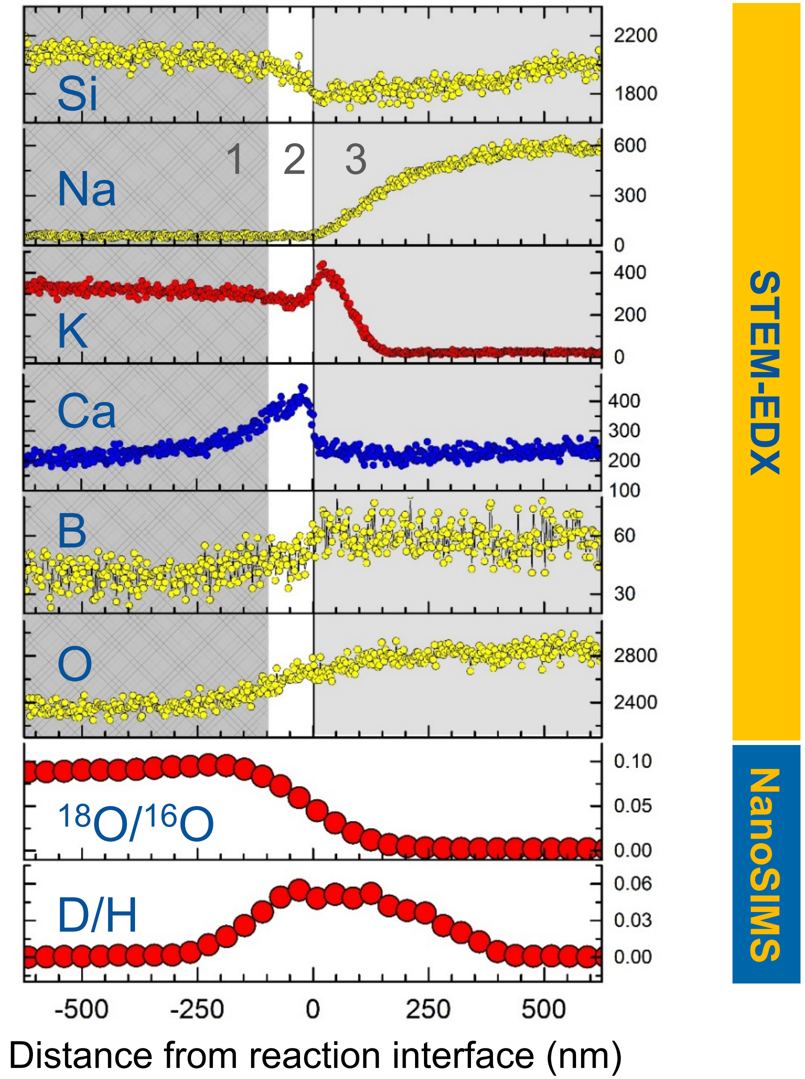
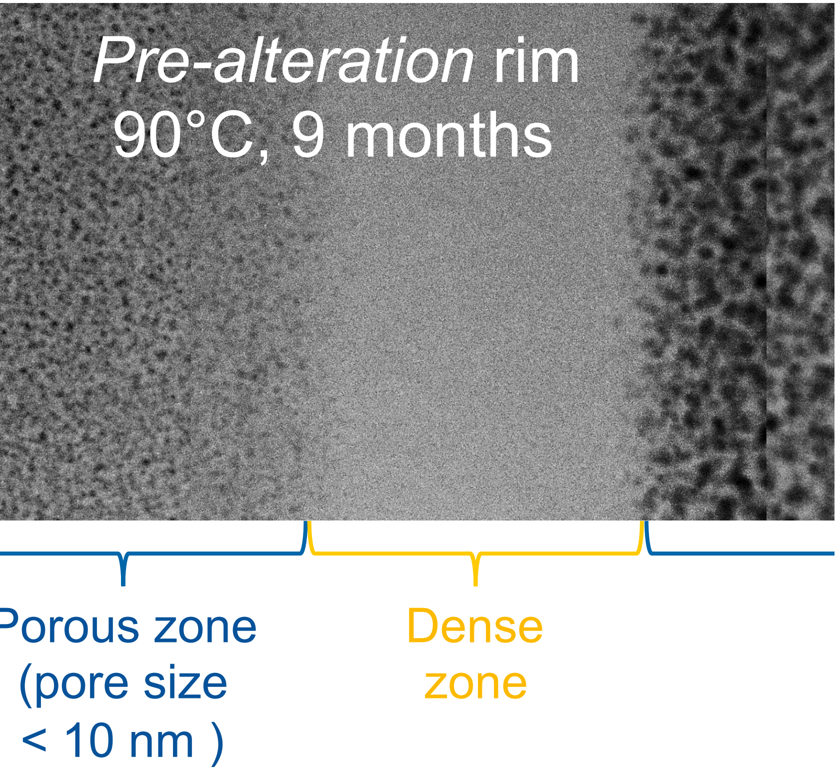
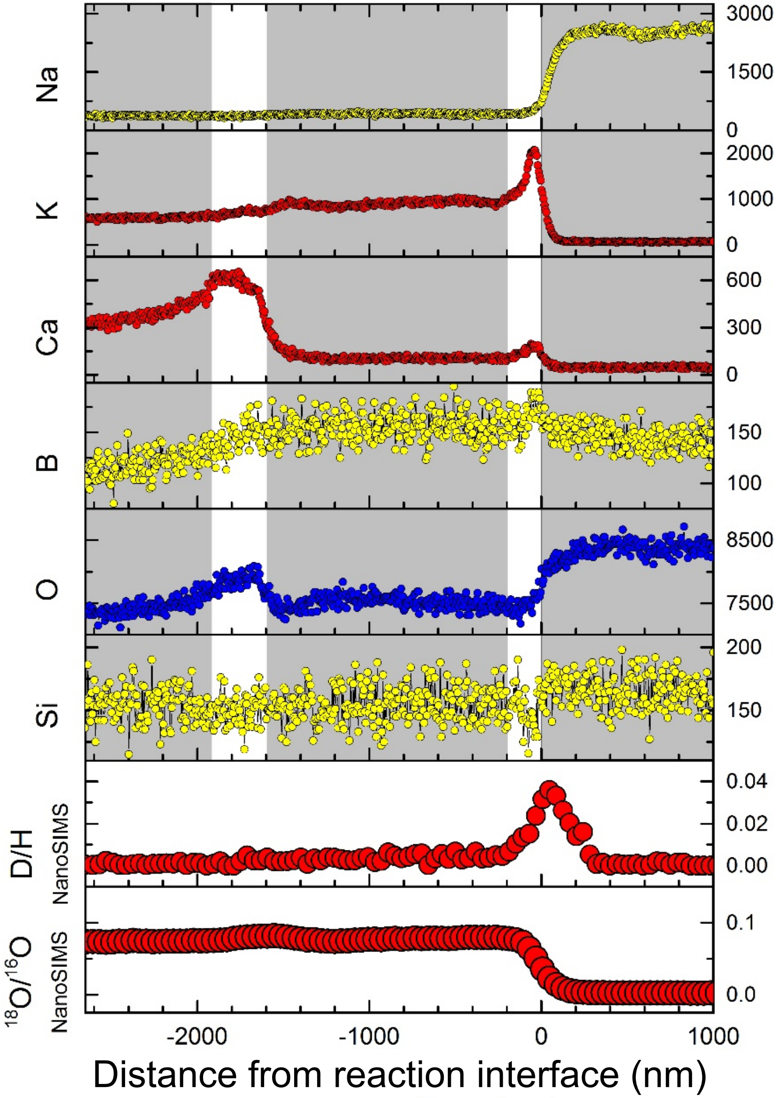


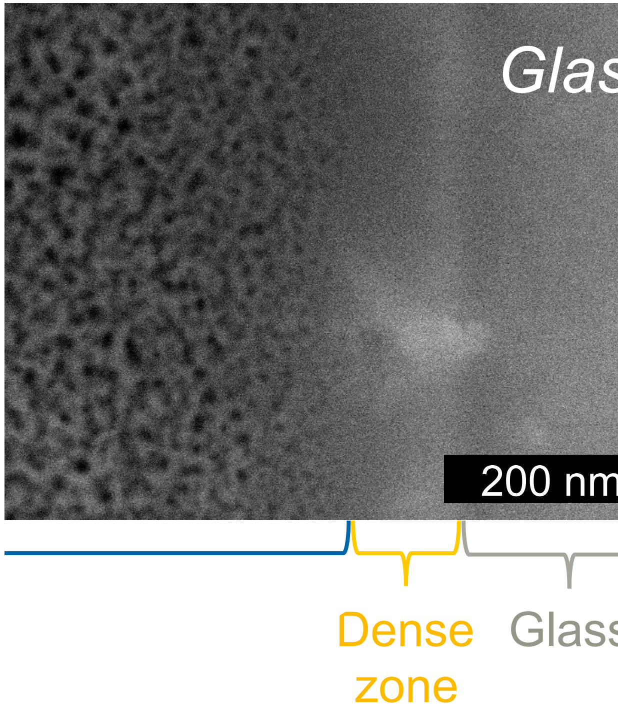


Results of isotope exchange experiments

perimental series #3: QBG, pre-altered at 90°C/150°C







Results of isotope exchange experiments

important conclusion:

The dense layers likely correspond to

(1) the water-rich zone or gab observed by *in-situ* Raman spectroscopy

(2) to the PRI (*Passivating Reactive Interface*) described by Frugier et al. (2008).

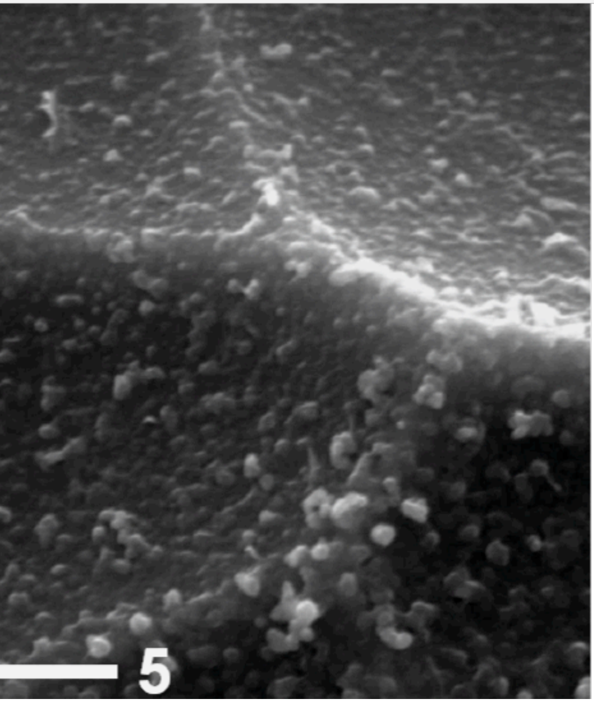
They most likely represents the product of a **quenched interfacial solution** (that is like highly supersaturated with respect to amorphous silica).

t follows, if true, that the reported dense layer **cannot be passivating** during the reacti

Other observations

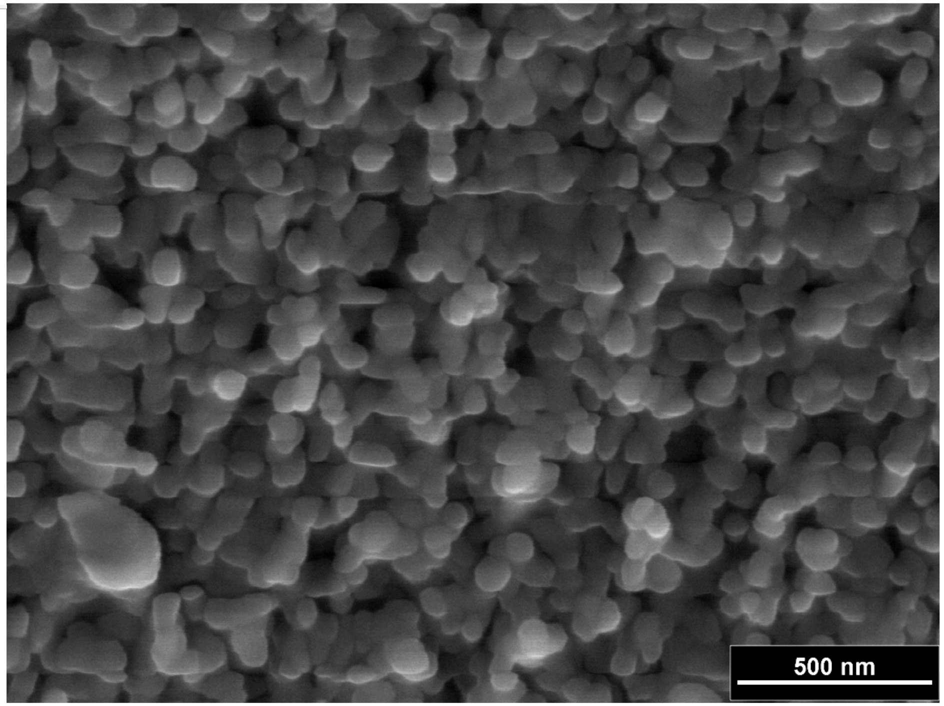
ilica layers formed in experiments with different glasses under different conditior

G: 90°C, 4 hours, $pH_{initial} \approx 7$



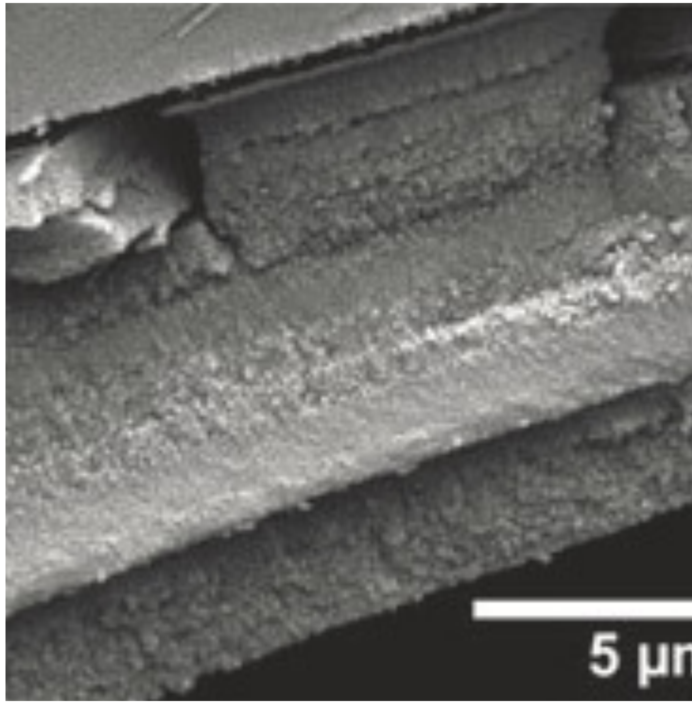
Geisler *et al.* (2015, GCA)

WAK: 150°C, 96 hours, $pH_{initial} \approx 0$



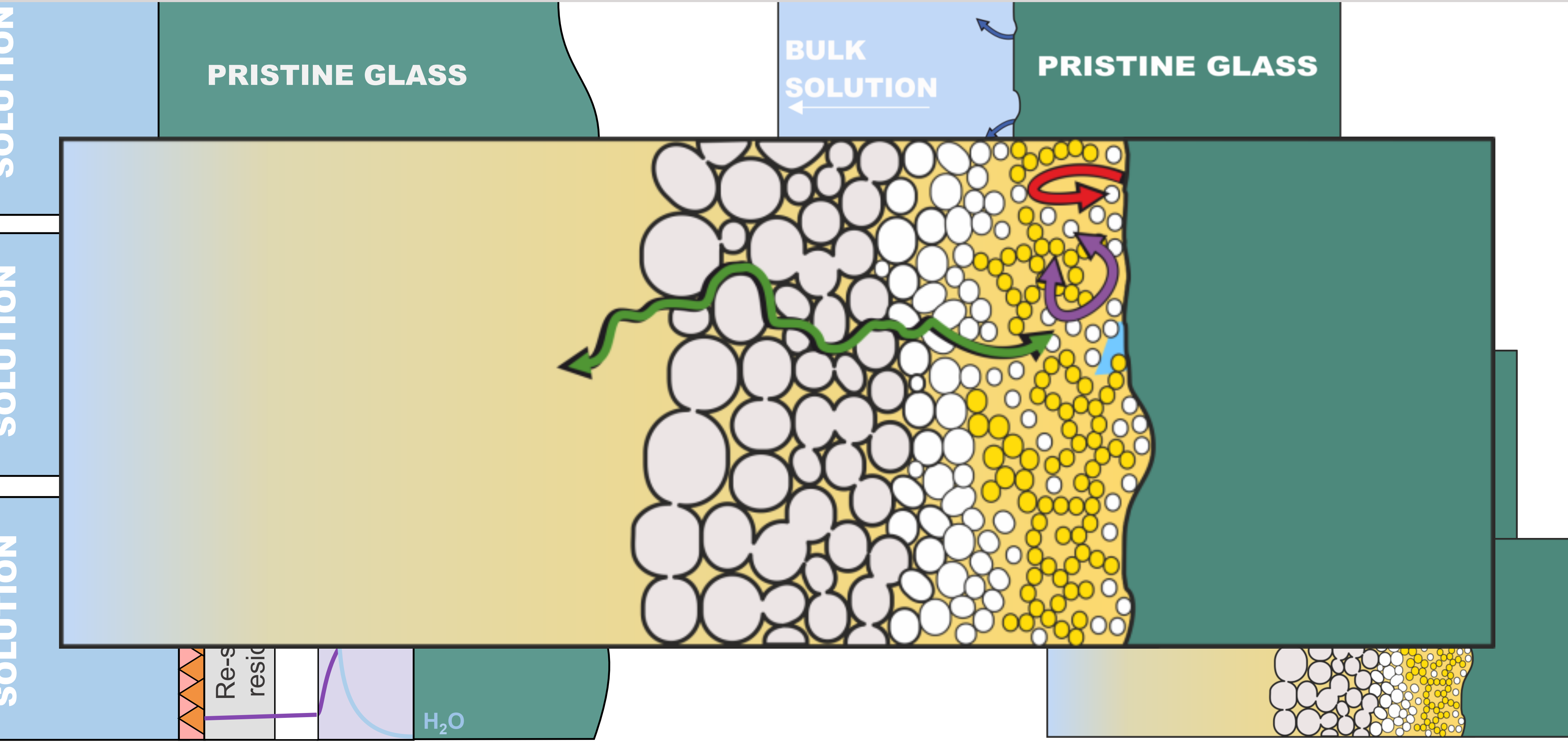
Geisler *et al.* (2010, J. Non-Cryst. Sol.)

CaKNaSi: 90°C, 260 hours, pH_{initia}



Dohmen *et al.* (2013, Int. J. Appl. Glass

Schematic drawing of the different layers after long-term glass-water contact

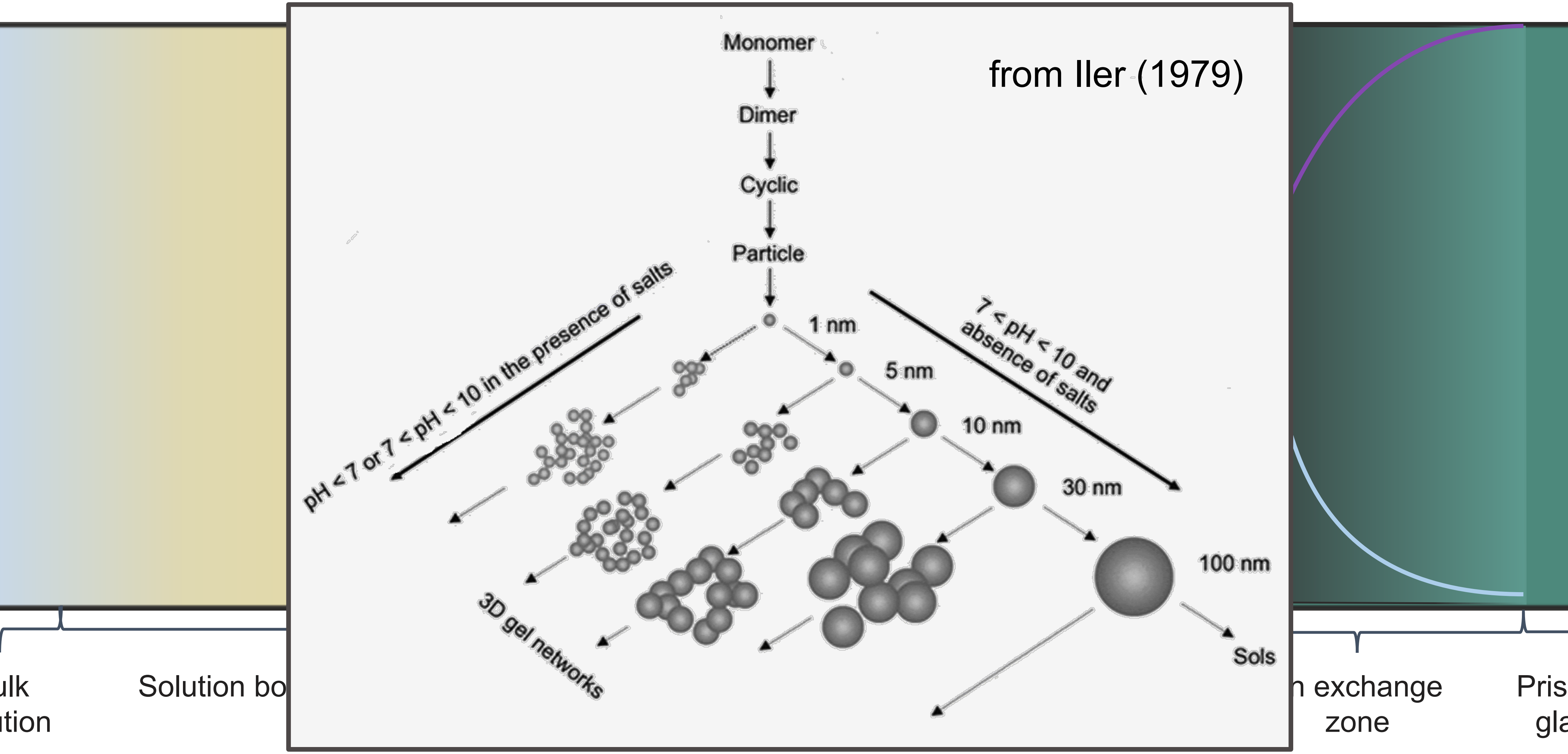


after Grambow (1986)

after Geisler et al. (2010; 2015)

Towards an unifying glass corrosion mechanism

Schematic drawing of the different layers after long-term glass-water contact



nclusions

owing reaction have been identified so far:

- **on exchange/interdiffusion** inside the glass (*diffusion-reaction process,* e.g., Doremus nodel).
- **Congruent dissolution** of the glass (incl. a number of individual microscopic reaction teps such as, e.g., hydrolysis).
- **Silica precipitation/deposition** from solution (incl. a number of individual microscopic eaction steps such as, e.g., condensation).
- **Silica aging** (e.g, polymerization, ripening).
- **Chemical transport** through the silica reaction layer (percolation controlled, anomalous
- **Precipitation of secondary minerals** within and at the silica surface (e.g., zeolites, ruti
- **Aqueous diffusion** within a solution boundary layer.

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and, last but not least,

you for your attention.

Conclusions

In silica undersaturated solutions, the glass initially **dissolves congruently**.

Once the solution at the surface boundary layer is saturated with respect to silica, silica will precipitate initially at the surface of the dissolving glass and later at preexisting silica aggregates → the reaction becomes **incongruent** and the glass is gradually replaced by amorphous silica along a **moving front**:

$$\textbf{Glass} + \mathbf{H_2O} \rightarrow \mathbf{SiO_2(am)}\downarrow + \mathbf{H_2O} + \textbf{Cations(aq)} \quad (+\,\Delta \mathbf{S})$$

The glass dissolution (r_d) and silica precipitation rate (r_p) have to be coupled:

$$r_d - (r_p + u) = 0,$$

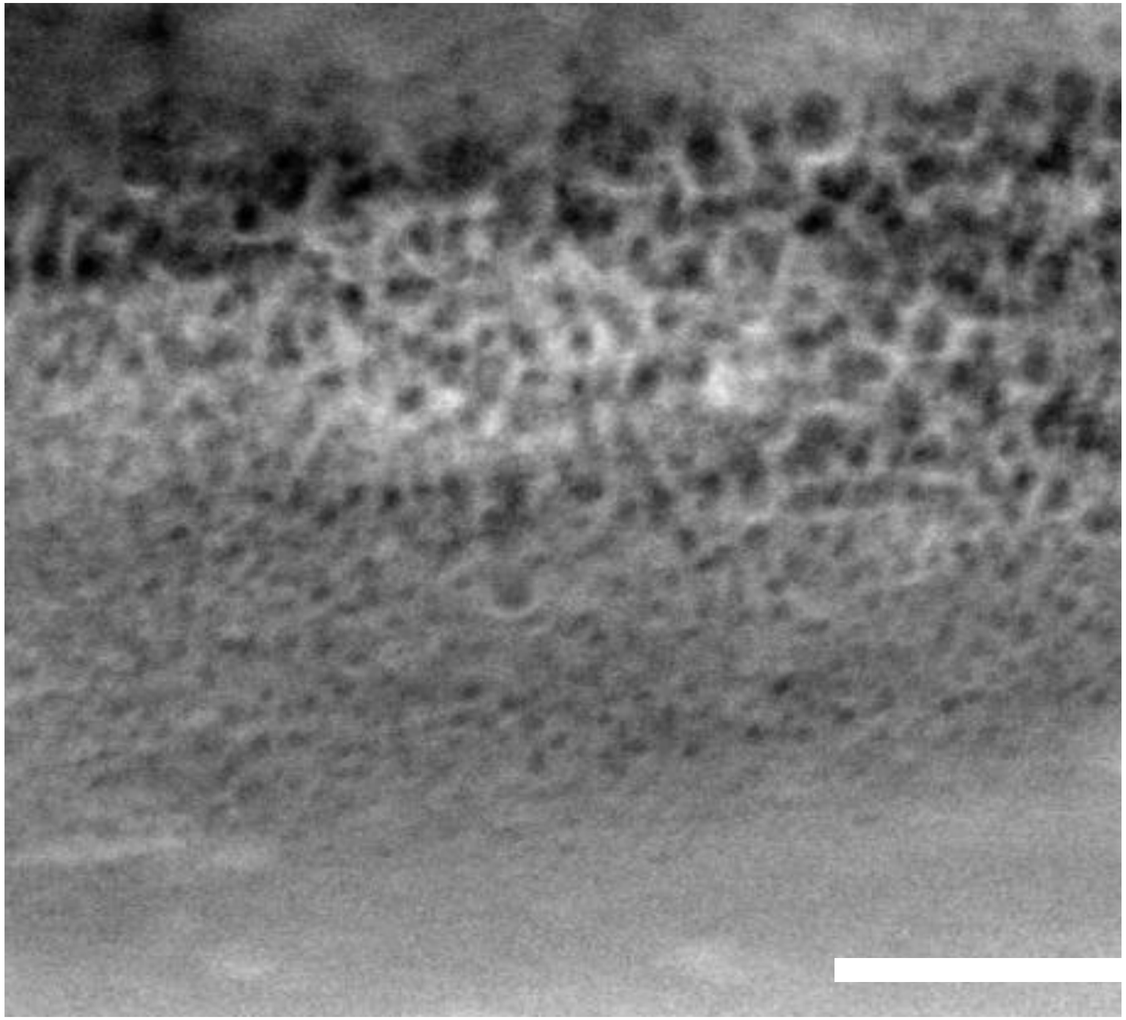
where u accounts for the quantities of elements that are released into solution per unit time.

The **thermodynamic driving force** for such an irreversible interface-coupled replacement reaction is give by the **solubility difference** between amorphous silica and the glass.

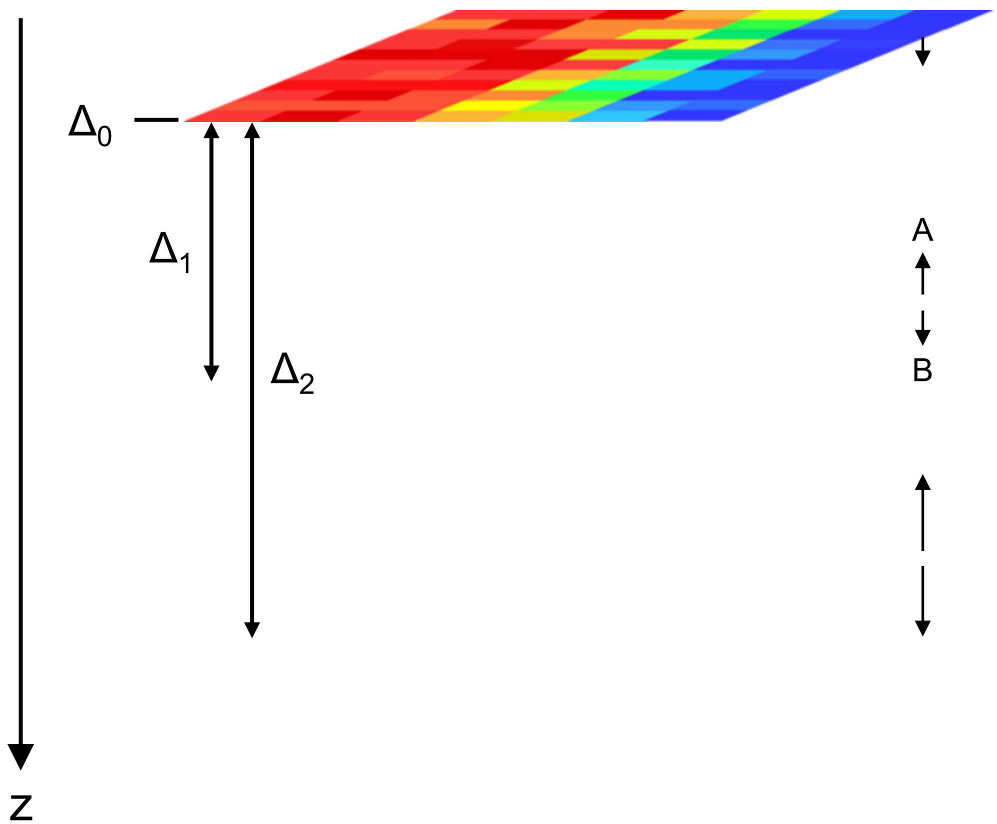
Complex, non-linearly coupled reactions at the interface along with chemical transport limitations due to th growing silica rim, which increasingly drives the system away from thermodynamic equilibrium, may cause the formation of **structural, porosity,** and/or **chemical patterns**.

An **ion exhange zone** may develop ahead of the dissolution-reprecipitation front. This diffusion-controlled process, however, is not directly rate-limiting.

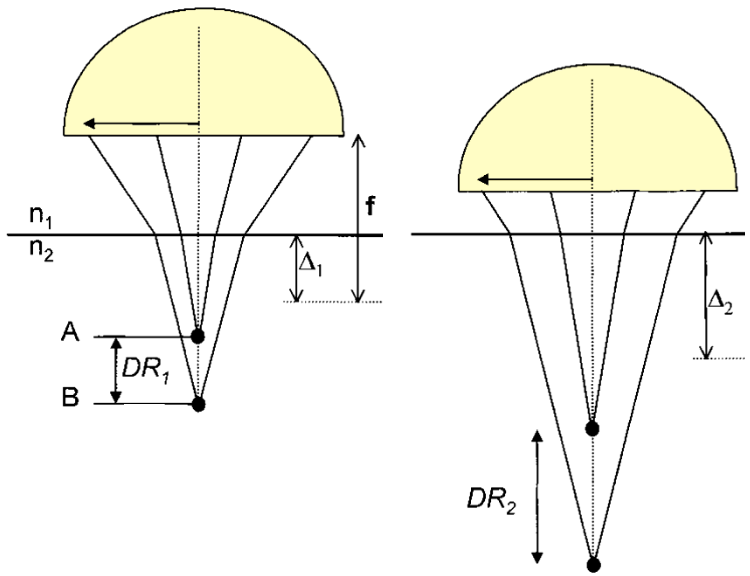
M tomography of porous zone (ISG , pre-altered 90°C/90°C, pH = 7)



atial resolution - A theoretical evaluation



	Lateral Resolution (*LR*)	Depth Resolution (*DR*)
	$LR_0 \approx 1.22\,\lambda / N.A.$	$DR_0 \approx 4\,\lambda / (N.A.)^2$
	$LR_1 = ?$	
	$LR_2 = ?$	



from Everall (2000)

atial resolution - An empirical evaluation