Evidences pour un nouveau mécanisme de corrosion des verres

Les Journées “Verres” Nice

18-20 November 2015

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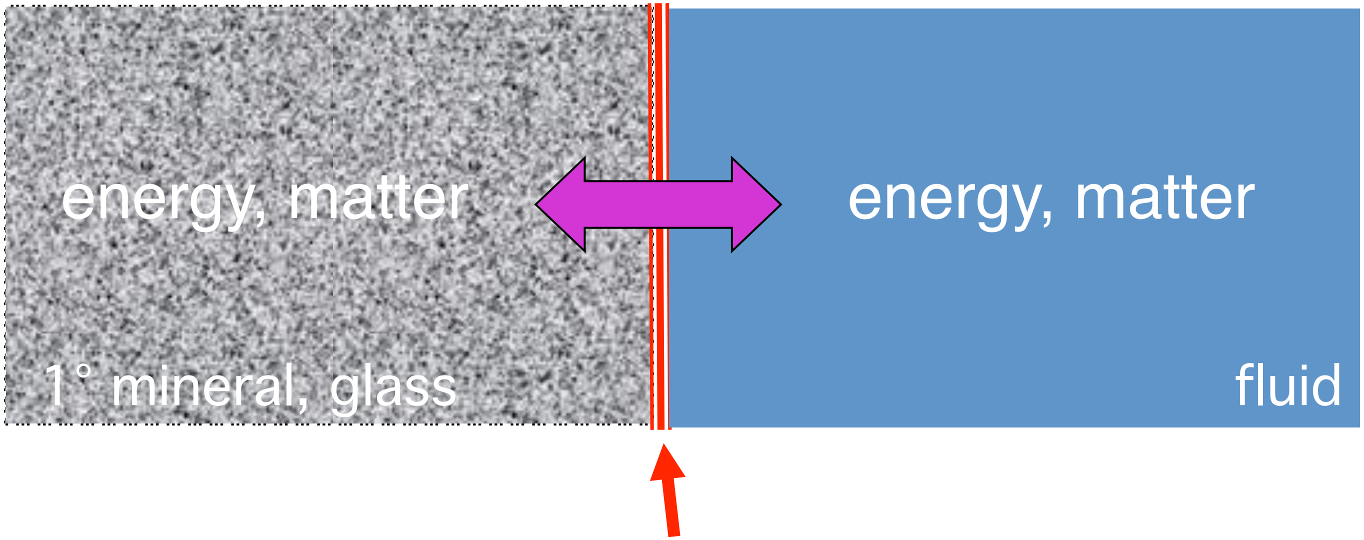
ISTerre
Institut des Sciences de la Terre

cnrs
advancing the frontiers

When a mineral-water or glass-water system tends to equilibrium, the interface is where all exchange of matter and energy occurs between fluid and solid

(dissolution, precipitation, oxidation/reduction, adsorption, absorption, ion exchange, catalysis)



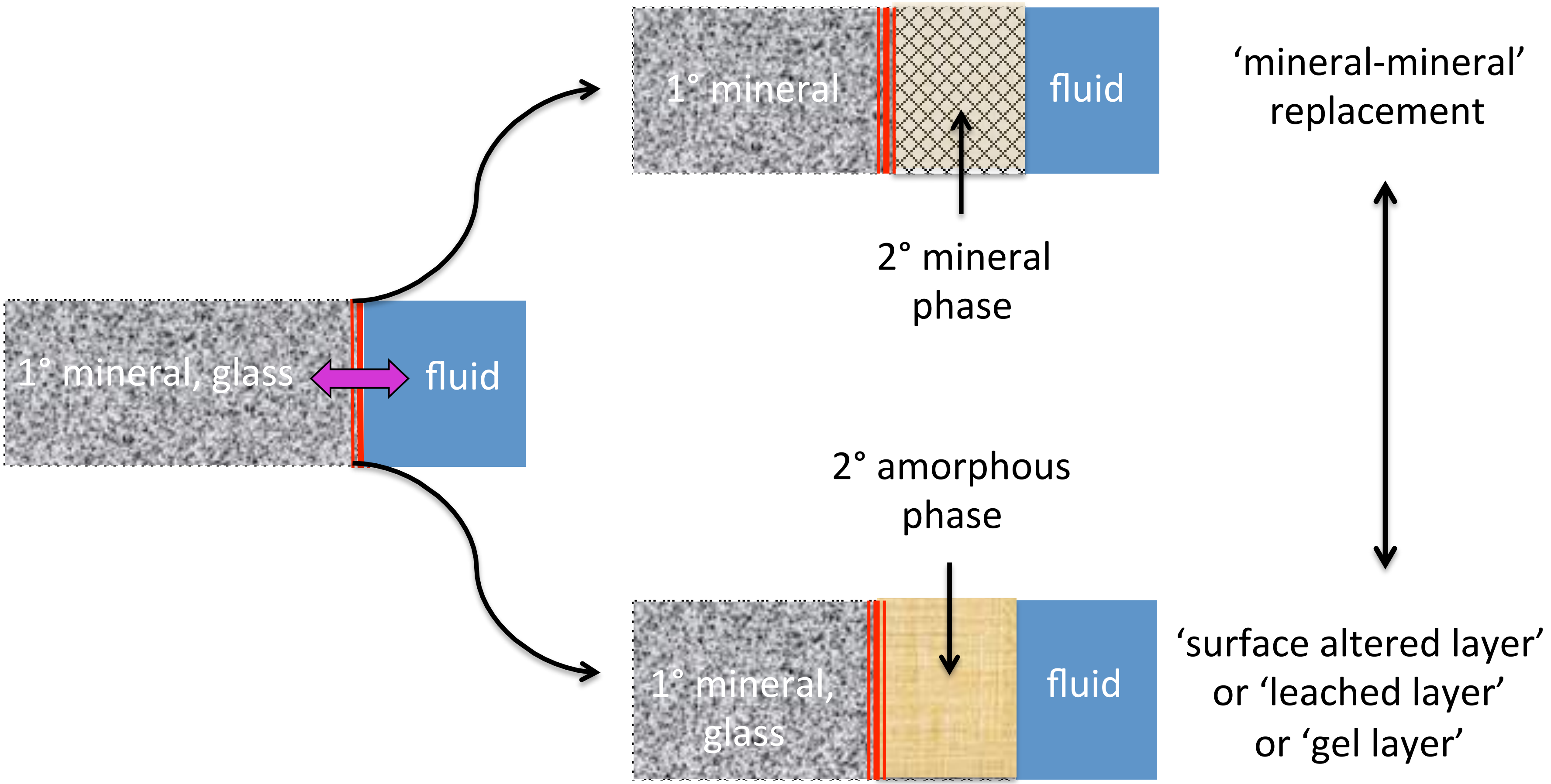
structural & chemical evolution of interface controlled by molecular-level reactions:

determining mechanism requires advanced analytical methods,
in particular nano to sub-nanometer probe sizes
combined with techniques having high mass resolution

Two main pathways for chemical weathering processes of 1° phase

what is the mechanism?

traditional view: non-stoichiometric dissolution by cation exchange/solid-state diffusion?



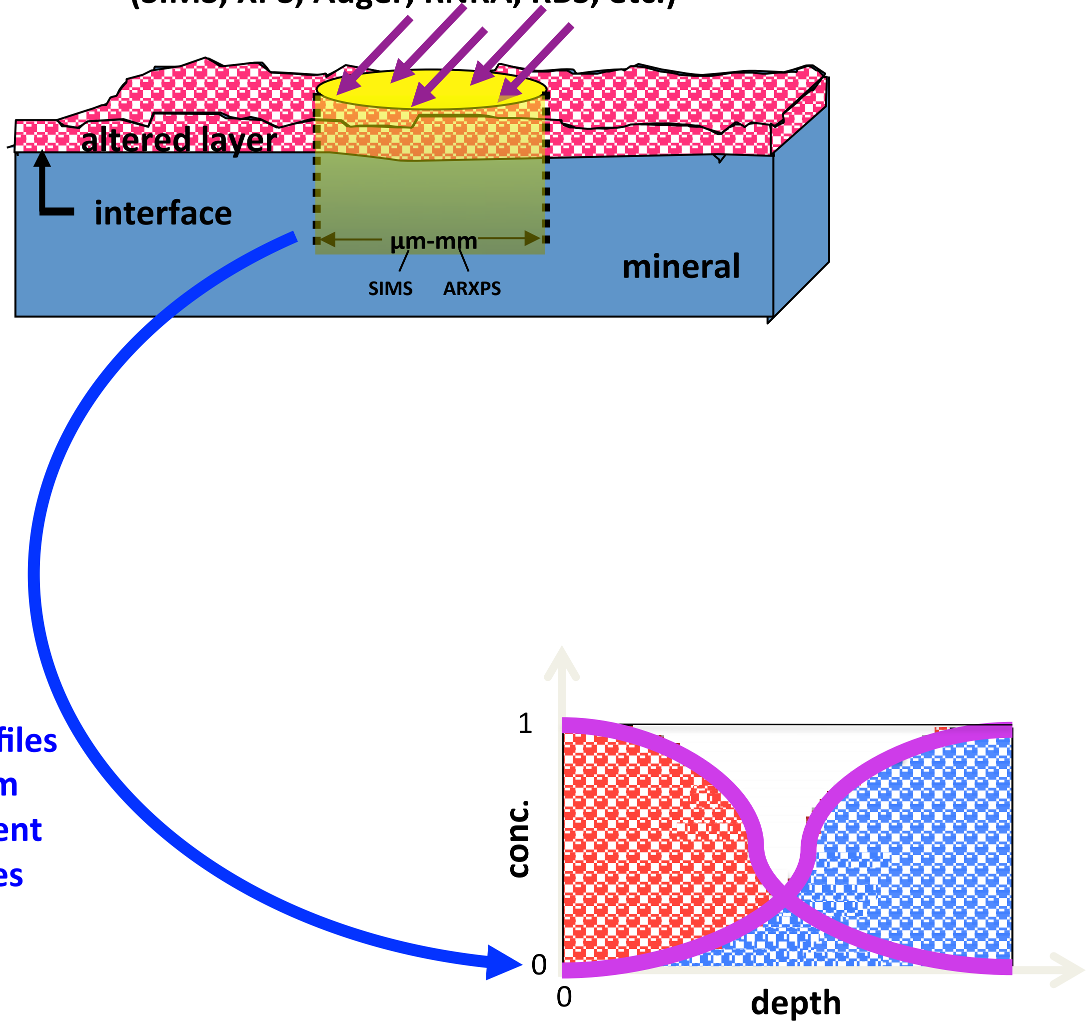
the more stable 2° phase has a different composition and/or structure

Probing non-stoichiometric altered surfaces: solid-state analyses

classical methods: (1970’s to present)

ion, X-ray, or electron beam incident to surface

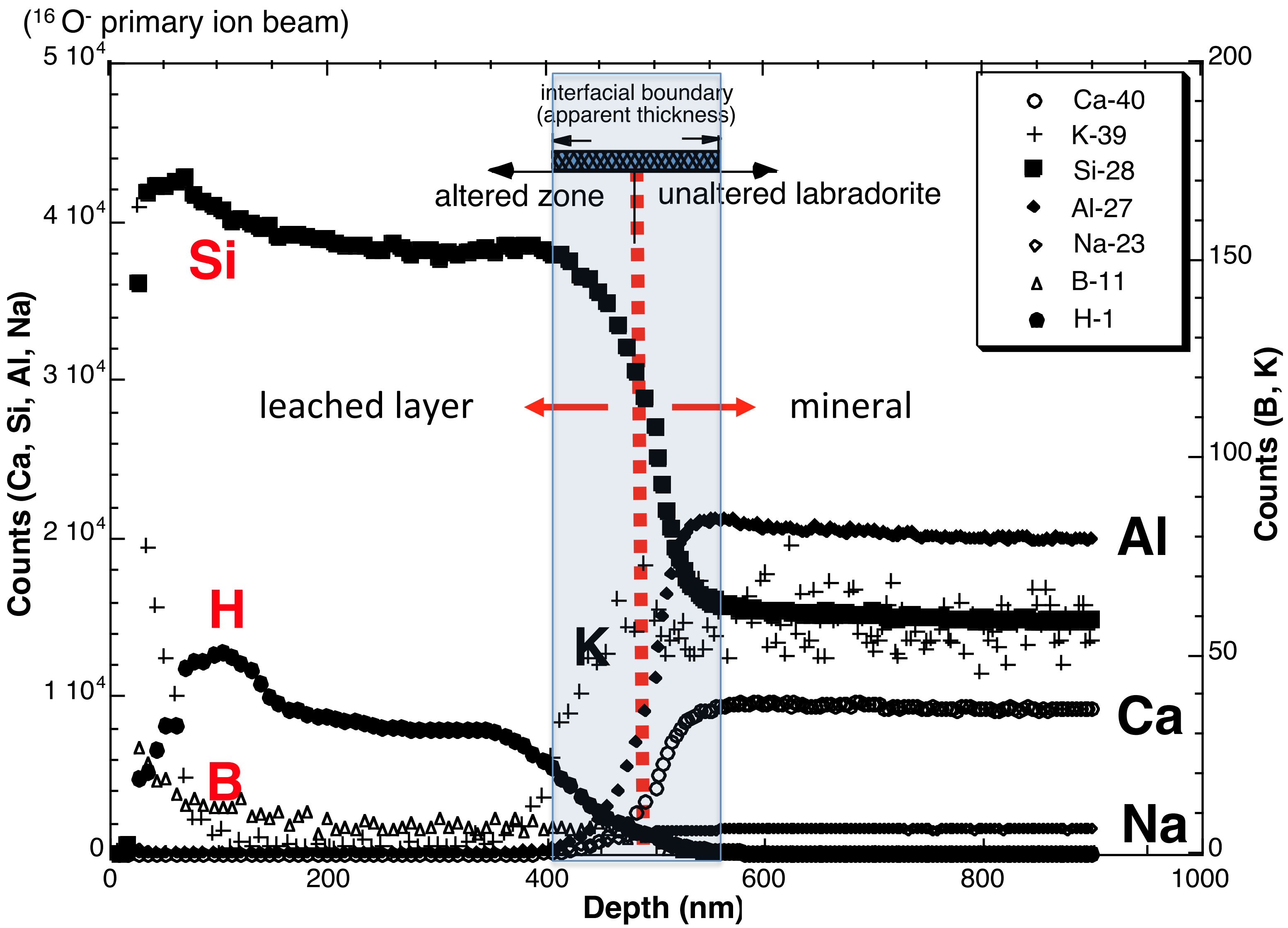
(SIMS, XPS, Auger, RNRA, RBS, etc.)



chemical profiles obtained from surface incident beam analyses

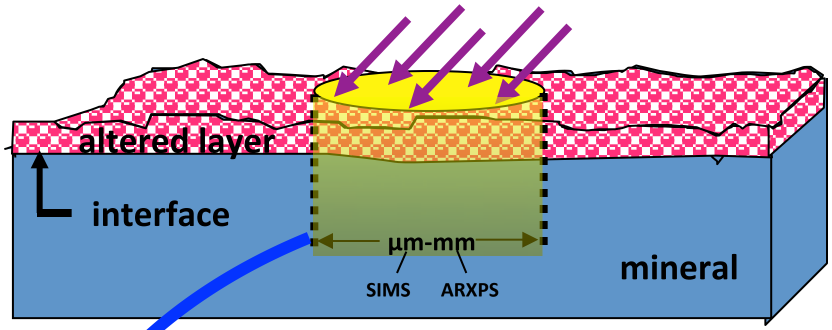
Leached layer and interfacial zone

SIMS depth profiles, labradorite feldspar, pH 1, 25°C

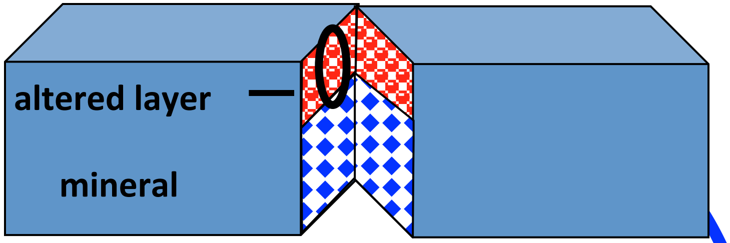


Probing non-stoichiometric altered surfaces: a different approach

classical method: (70's to present)
Ion, X-ray, or electron beam incident to surface



new method: prep. in cross section
FIB or ultramicrotomy

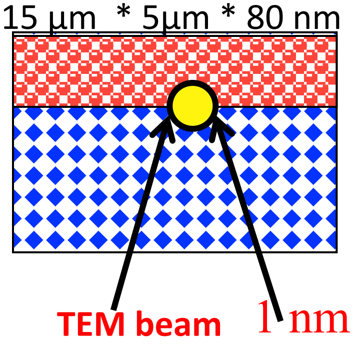


μm-mm beam size (poor lateral resolution)
chemical 'profiles' are modified:

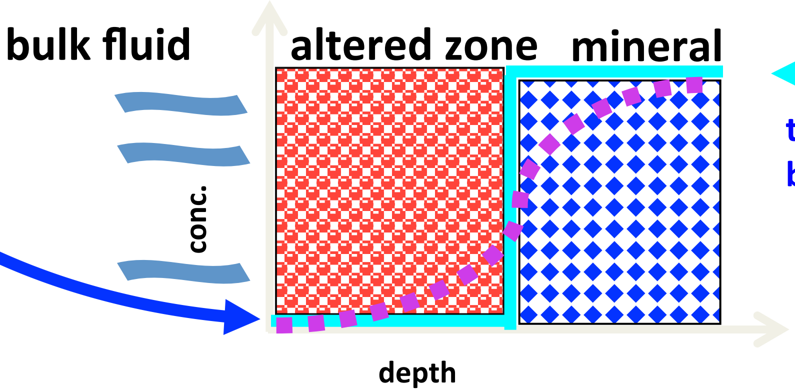
a) **convolution effect (true profile + topography)**
b) **ion beam-target atom interactions**

nm-sized TEM probe
meas. chemical profiles <u>directly</u>

ultrathin FIB-TEM foil



true profile, by FIB-TEM



profile obtained by surface incident beam

MATERIALS SCIENCE

Why Mineral Interfaces Matter

Andrew Putnis

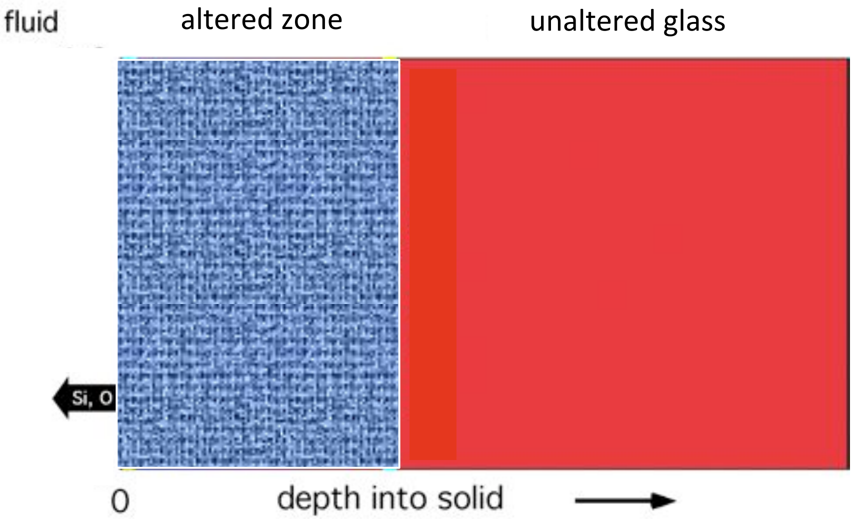
SCIENCE VOL 343 28 MARCH 2014
Published by AAAS

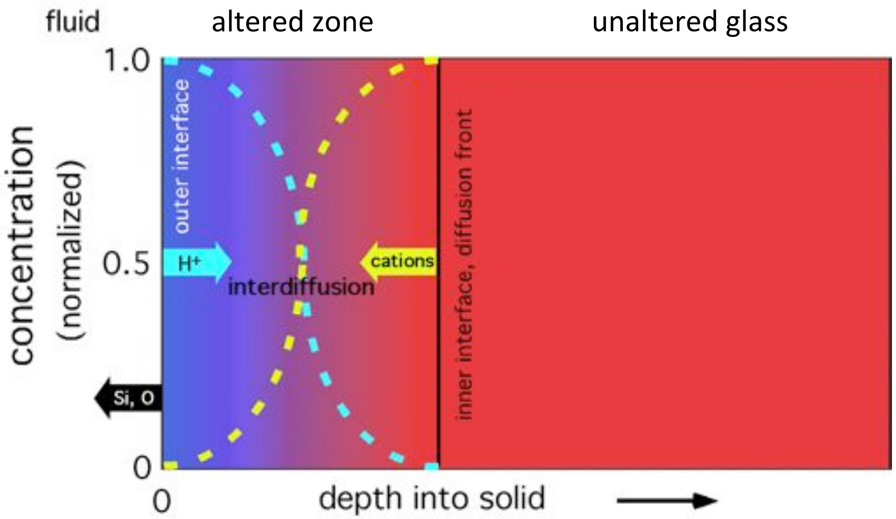
Reactions at mineral-fluid interfaces play a key role in processes ranging from the deep Earth to materials synthesis and nuclear waste storage.

> “The mechanism of leaching has been the subject of debate, especially in relation to chemical weathering on Earth, with the consensus moving toward a dissolution-precipitation mechanism as opposed to diffusional exchange (Hellmann et al. 2012).”

Models of glass corrosion

(after Dran et al., 1986)



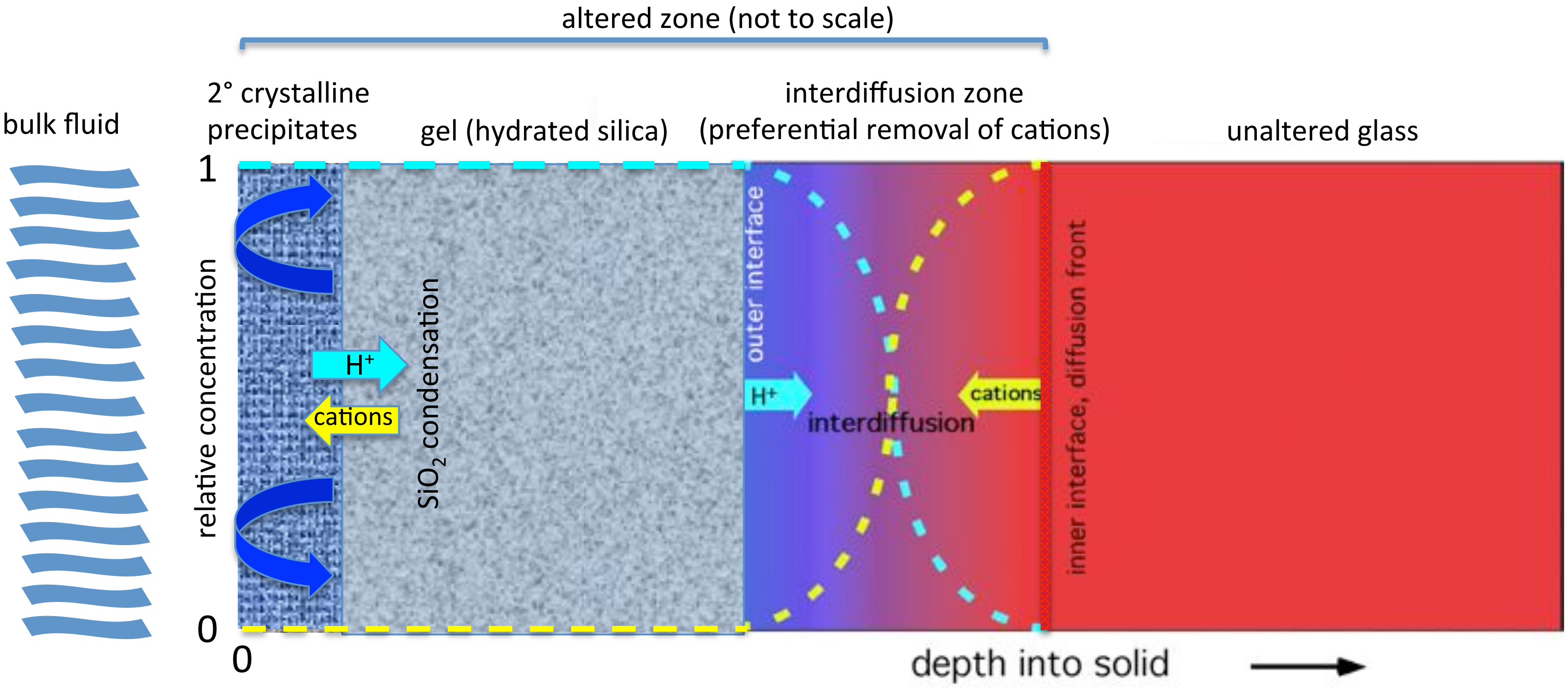


Model 1a
complex glasses & natural systems:
precipitation of 2° crystalline phases
from dissolved constituents of glass

Model 1b
chemically simple glasses:
in situ transformation via selective
cation removal by interdiffusion

Current model of glass corrosion

(adapted from the glass literature)



Current accepted mechanism:
in situ transformation via selective
cation removal by interdiffusion;   at greater reaction progress (ξ)
a gel layer forms by hydrolysis/condensation reactions +
re-adsorption of silica from bulk fluid;
secondary crystalline phases may precipitate on top of gel

MATERIALS SCIENCE

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“The mechanism of leaching has been the subject of debate, especially in relation to chemical weathering on Earth, with the consensus moving toward a dissolution-precipitation mechanism as opposed to diffusional exchange (Hellmann et al. 2012).”

“The same questions concern the mechanism of aqueous alteration of glass used to encapsulate radioactive nuclear waste. The currently accepted models, based on diffusional exchange of ions between the glass and the solution, are being challenged by new models based on coupled dissolution-precipitation mechanisms (12).”

Laboratory corrosion of SON 68 glass

(inactive analog of French R7T7 nuclear glass)
ANDRA post-doctoral contract

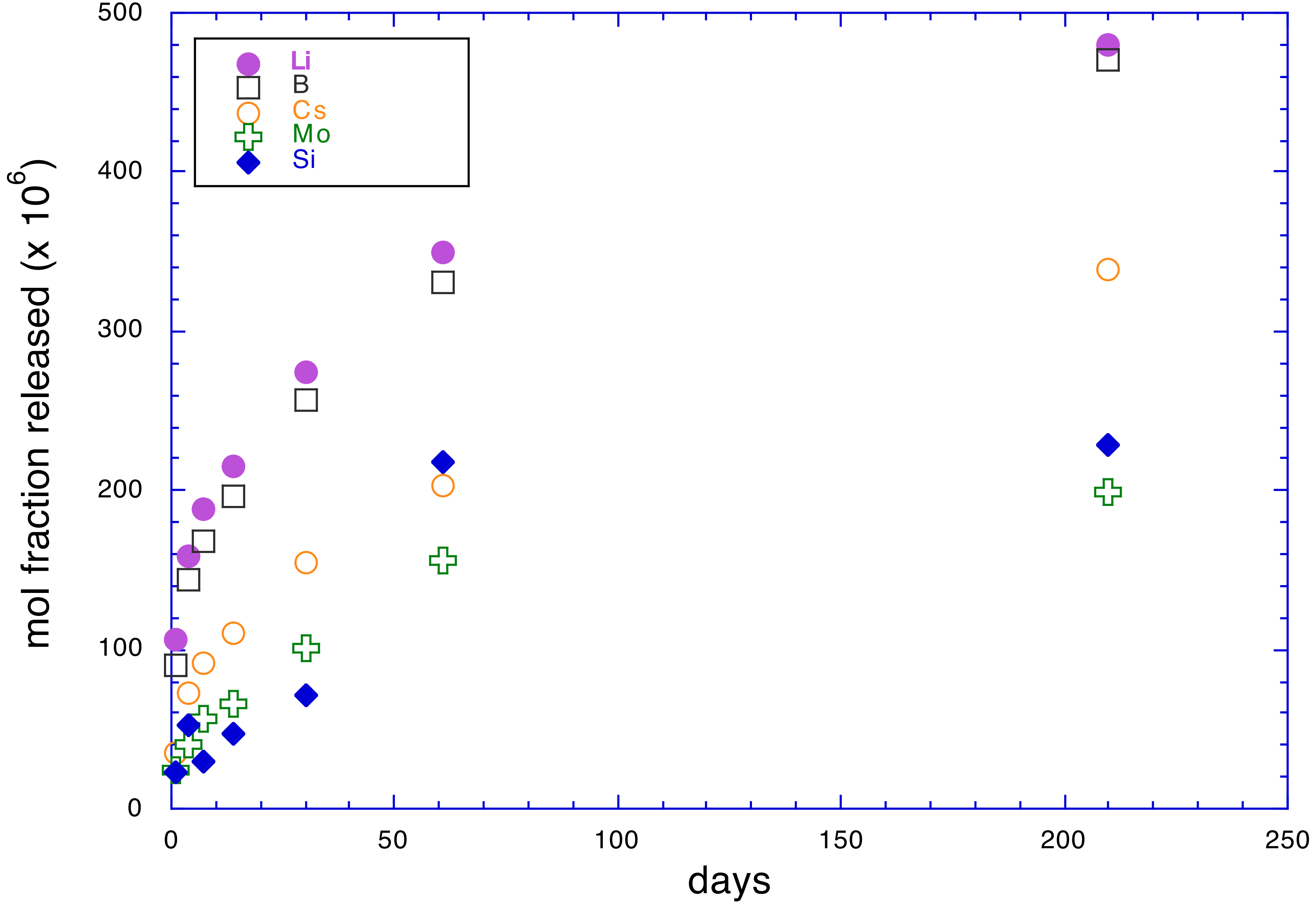
Chemical composition of glass (wt %):
SiO_2 = 45.48, B_2O_3 = 14.02, Na_2O = 9.86, Al_2O_3 = 4.91, CaO = 4.04, Fe_2O_3 = 2.91, ZrO_2 = 2.65, ZnO = 2.50, Li_2O = 1.98, 21 other cation oxides = 11.65).
(framework cations and interstitial cations)

Duration:
a. 4 days, 1 month, 3 months, 7 months, 50 °C: corrrosion by Subatech, Nantes
b. 10 and c. 26 years, 90 °C: corrosion by CEA-Marcoule

Experimental conditions:
a. 50 °C, water at circumneutral pH, static reactors, S/V = 0.1 cm^{-1} (monolith)
b. 90 °C, water at circumneutral pH, S/V de 600 cm^{-1} (powder grains < 40 µm)
c. 90 °C, granitic water, glass surrounded by silica sand + granite grains

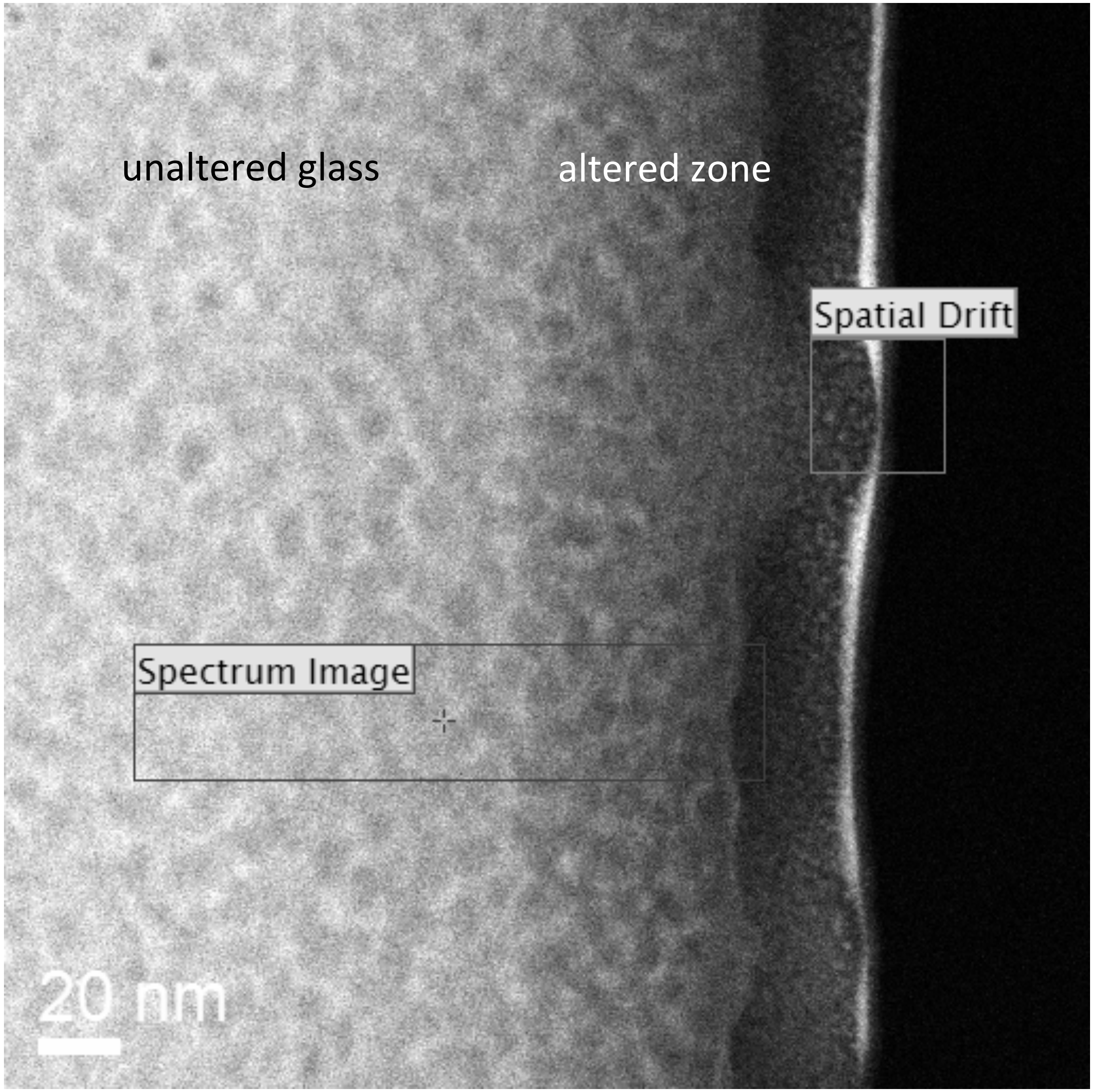
Aqueous chemistry measured during glass corrosion

apparent non-stoichiometric dissolution



STEM-HAADF image of surface altered layer

(ESTEEM1, Oxford Materials Dept.)

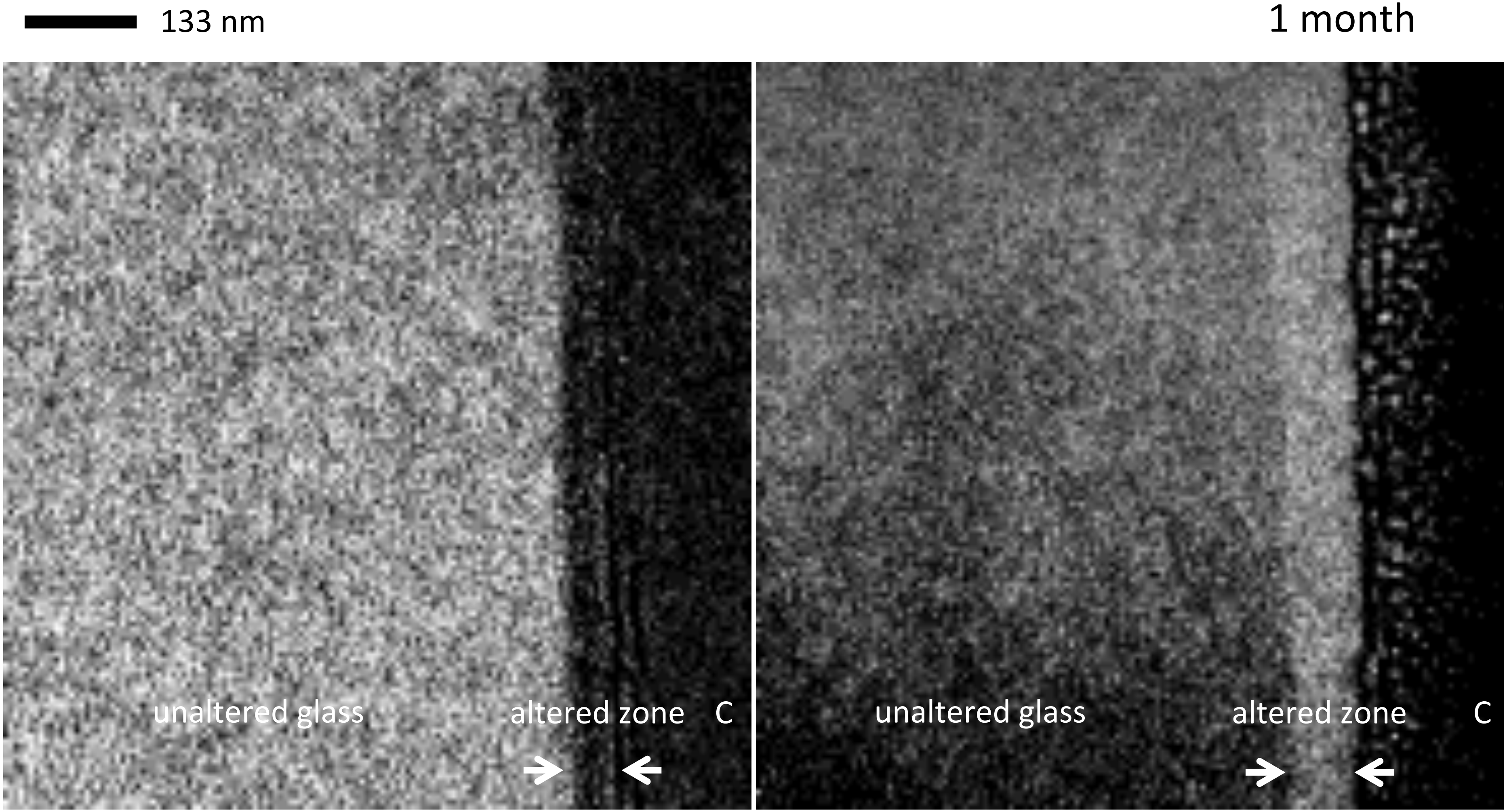


1 month

1 month
$[SiO_2]_{expt} << [SiO_2]_{am\ silica}$

EFTEM image

(ESTEEM, Kavli Inst. Nanosciences Delft, NL)



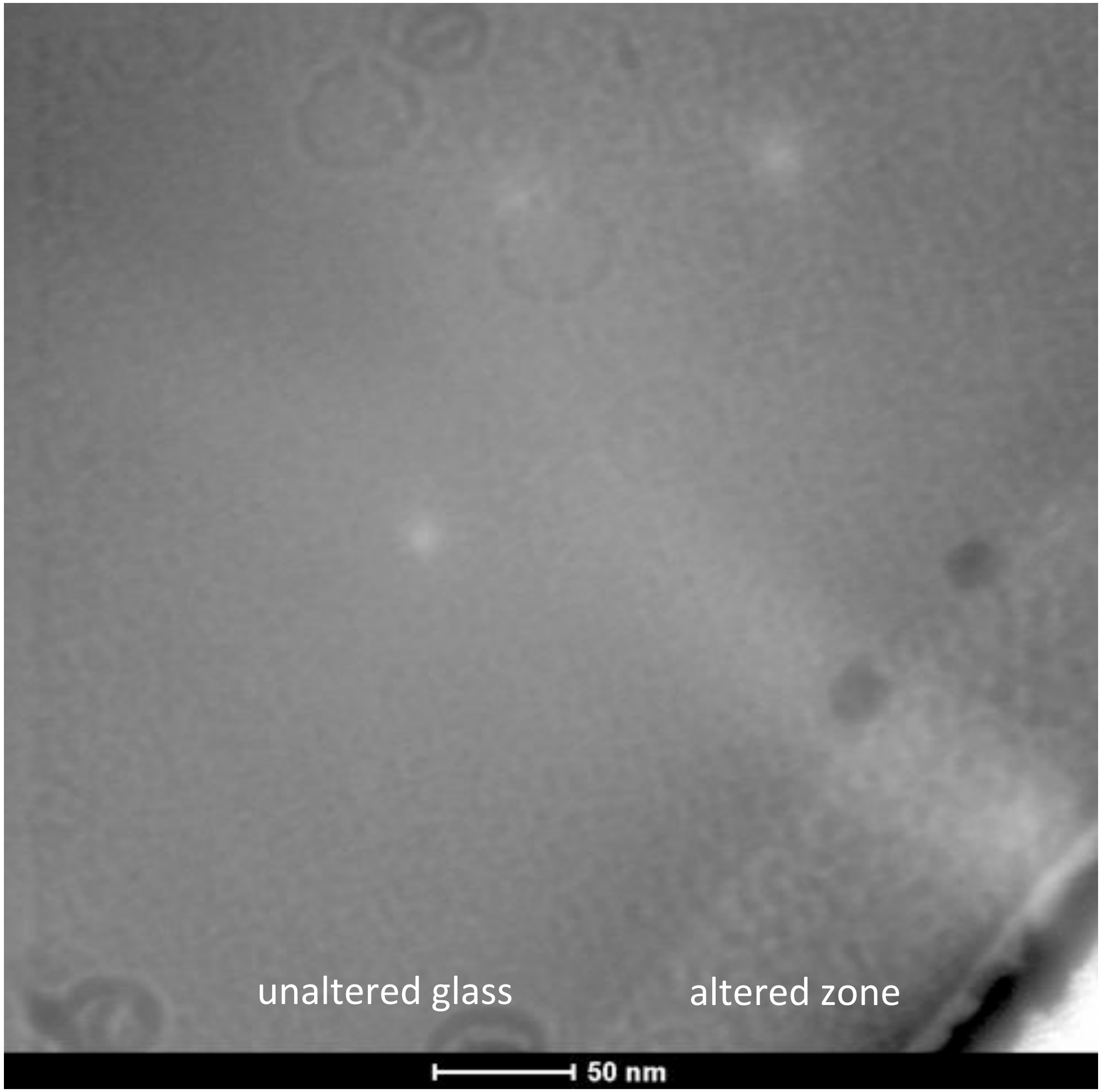
1 month

B map

Si map

STEM-HAADF image of altered glass

(ESTEEM, Kavli Inst. Nanosciences Delft, NL)



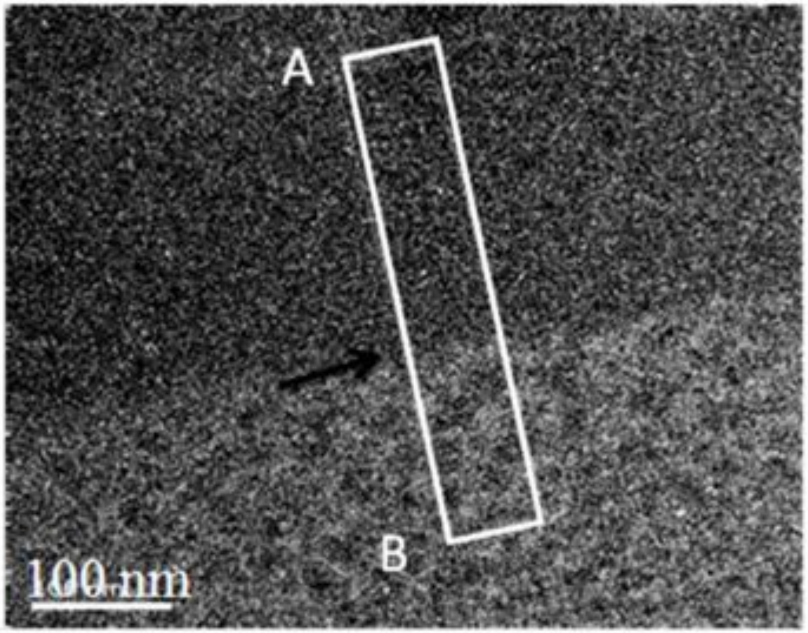
7 months

$[SiO_2]_{expt} << [SiO_2]_{am\ silica}$

Energy filtered TEM image and profile for boron

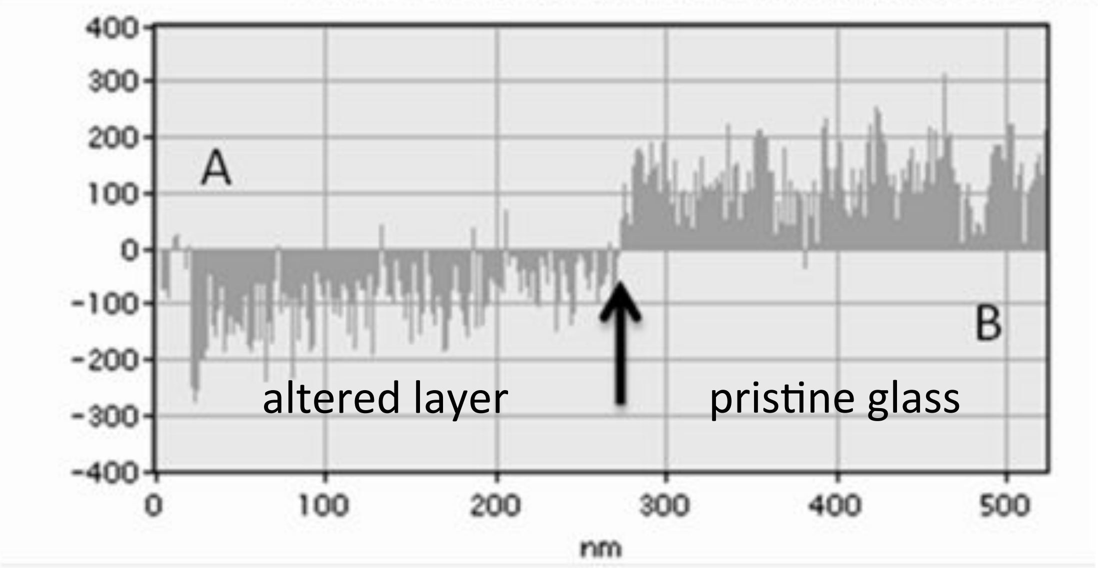
(Univ. of Münster)

10 years



altered layer,
B-depleted

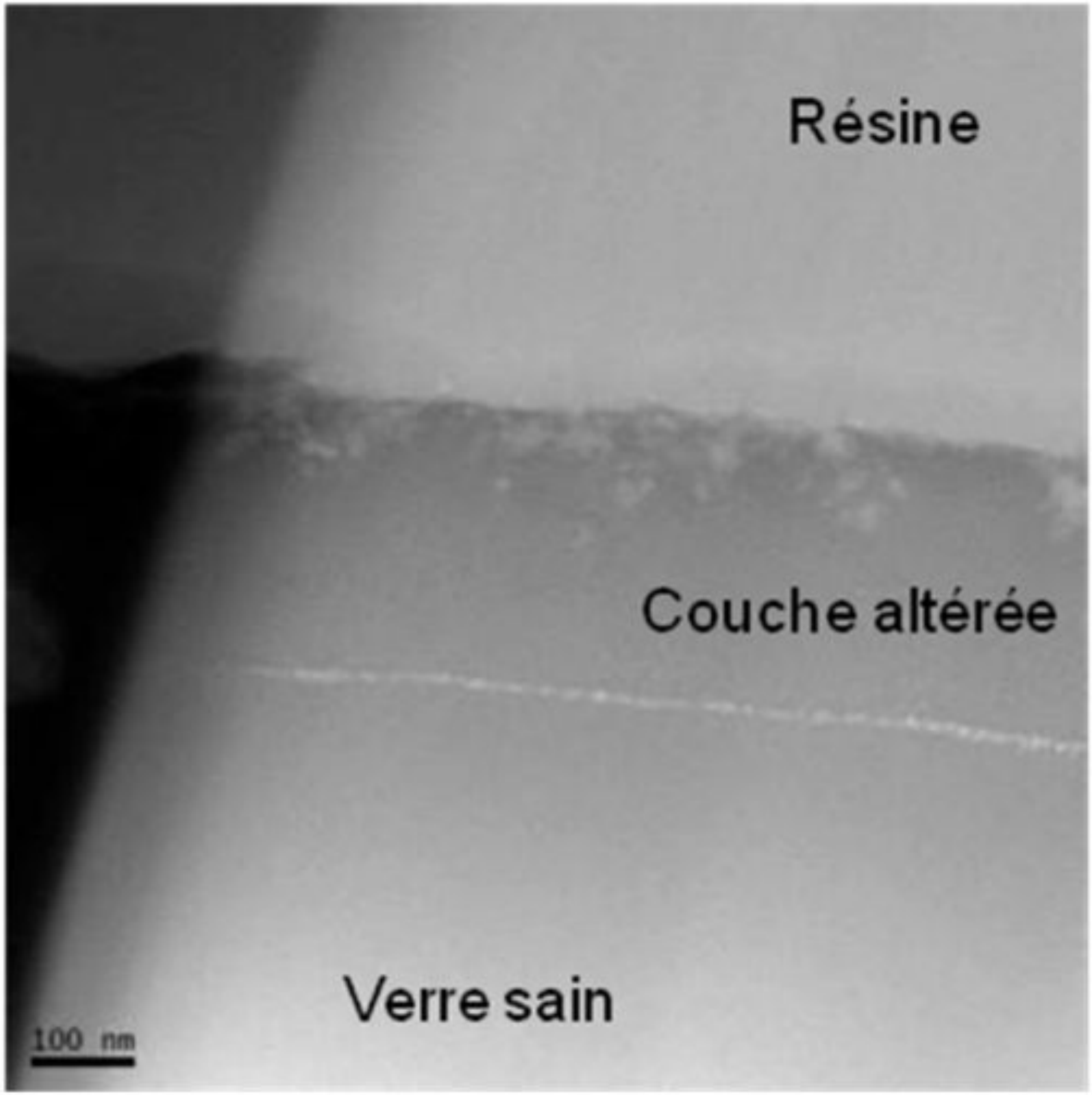
pristine glass
containing B



BF image

(Univ. of Münster)

10 years



resin

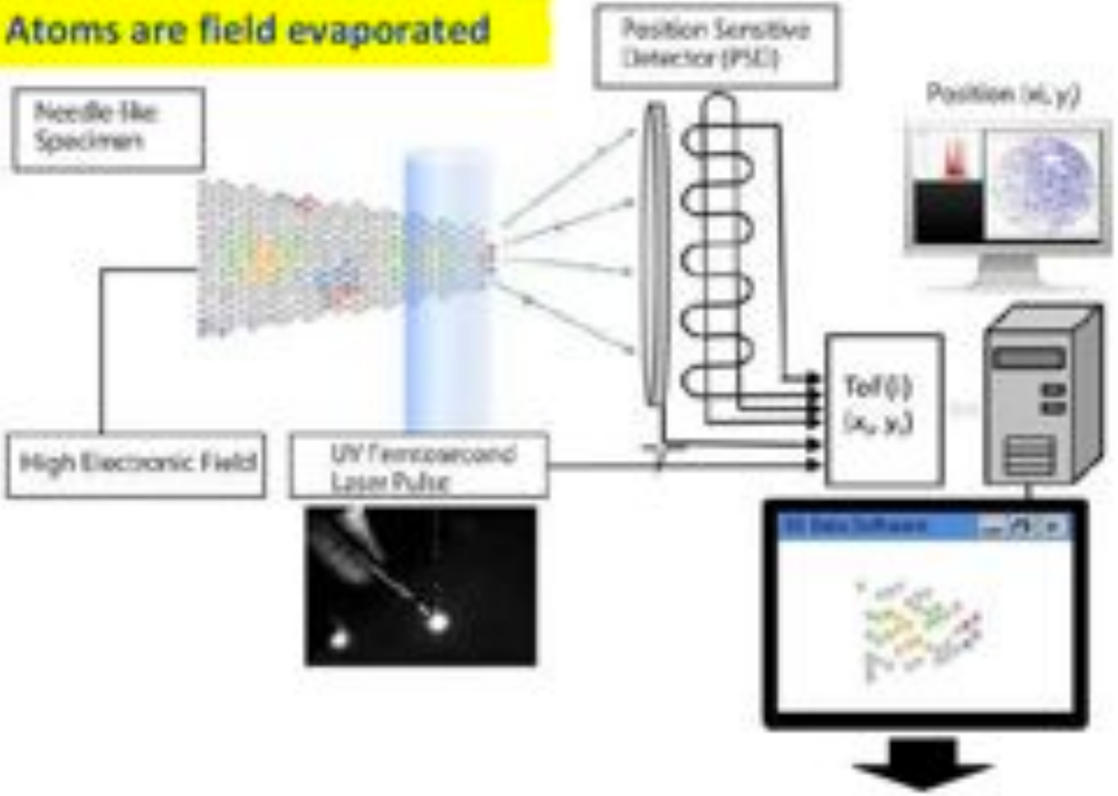
altered layer

pristine glass

Atom probe tomography

E. Cadel, GPM, Rouen
Expérience METSA12 A48 réalisée au GPM
laser assisted 3DAP CAMECA-LaWaTAP

Atoms are field evaporated



Position sensitive detector

→ 3D mapping of atoms

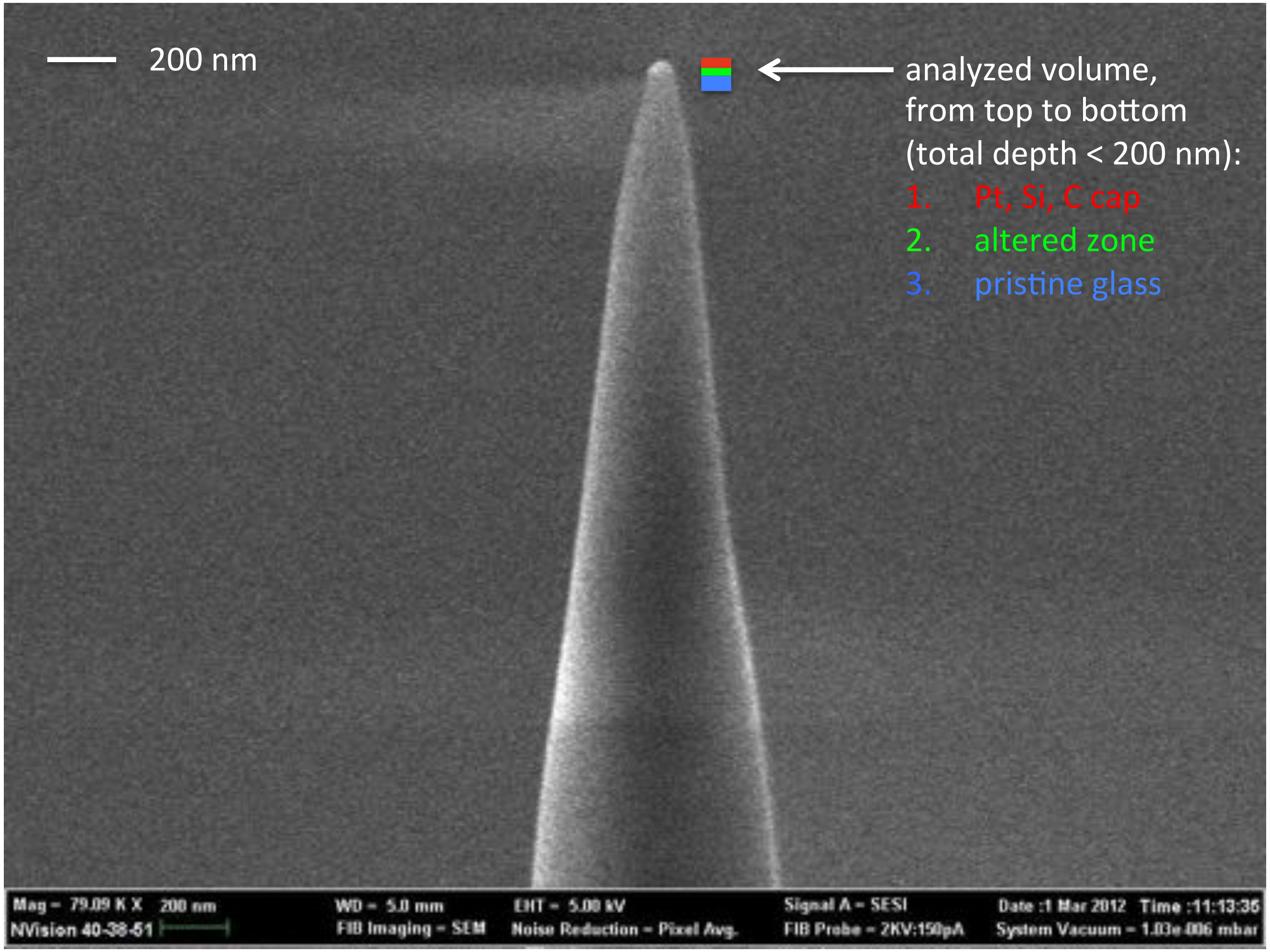
Time of flight mass spectrometry

→ Chemical information

Mapping at the atomic scale of
the 3D spatial distribution of atoms in the sample
(Depth resolution = 0,1 nm and lateral resolution ~ 0,3 nm)

Atom probe tomography applied to glass corrosion

FIB-prepared 1-month altered glass, tip radius 50-100 nm



analyzed volume, from top to bottom (total depth < 200 nm):

1. Pt, Si, C cap
2. altered zone
3. pristine glass

Advantages:

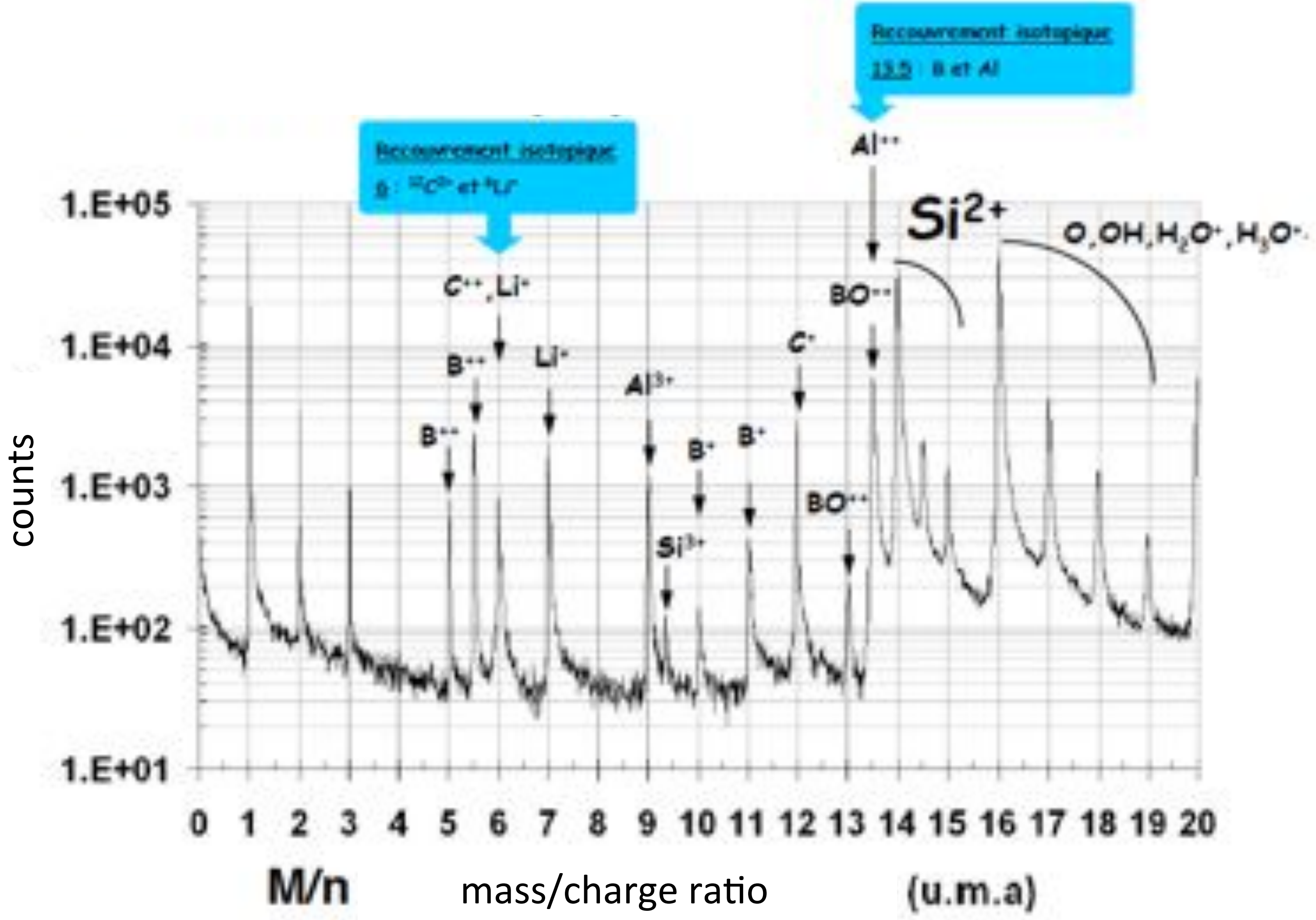
1. spatial resolution
2. mass resolution
   $m/\Delta m = 1000$
3. same analytical efficiency
   for heavy & light elements
   (> 10 ppm)
4. 3D tomography

Disadvantages:

1. small analysis volume
2. non-conducting samples
3. fragility of sample
4. sample preparation

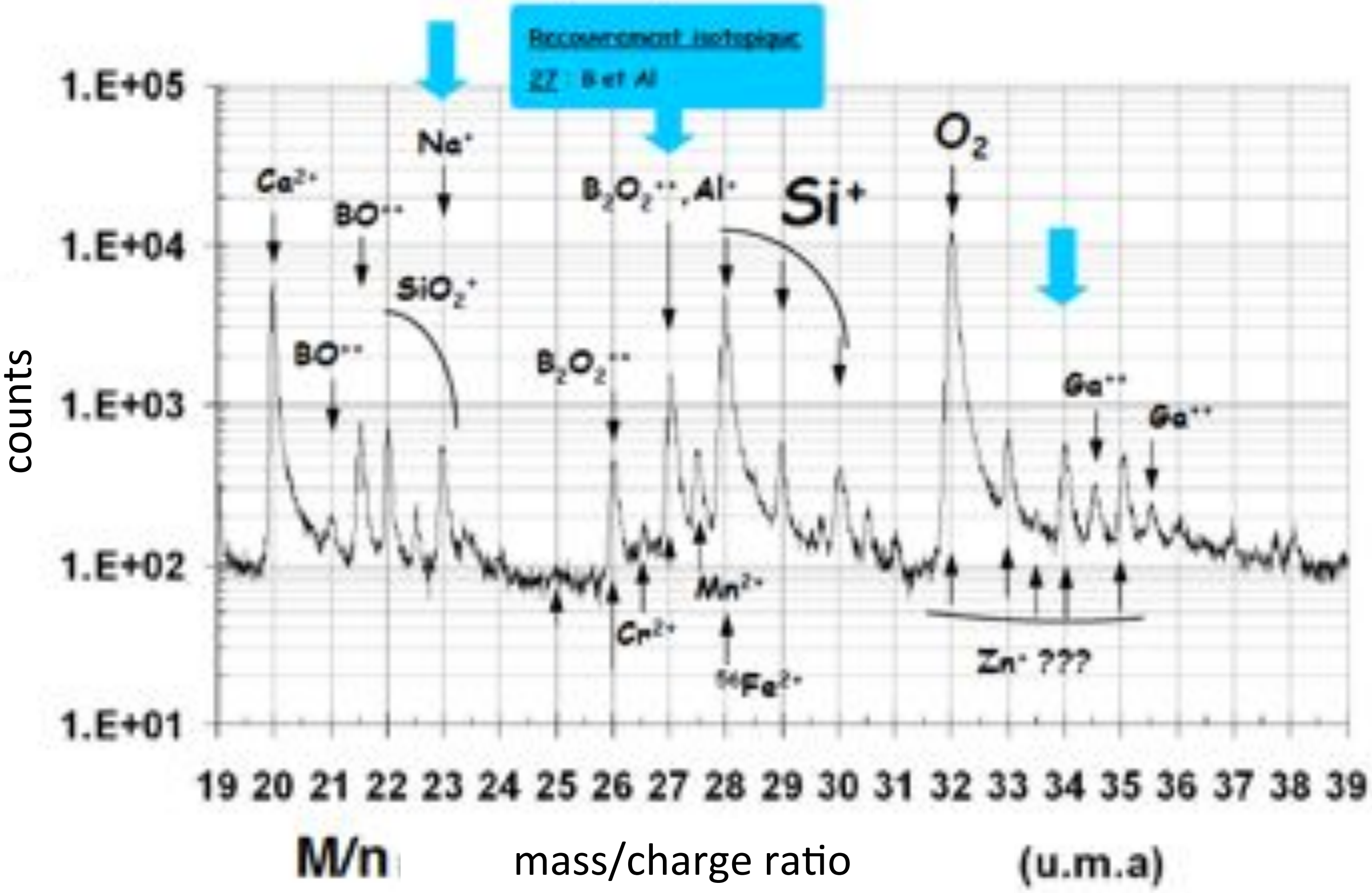
Atom probe tomography: mass (isotope) spectra

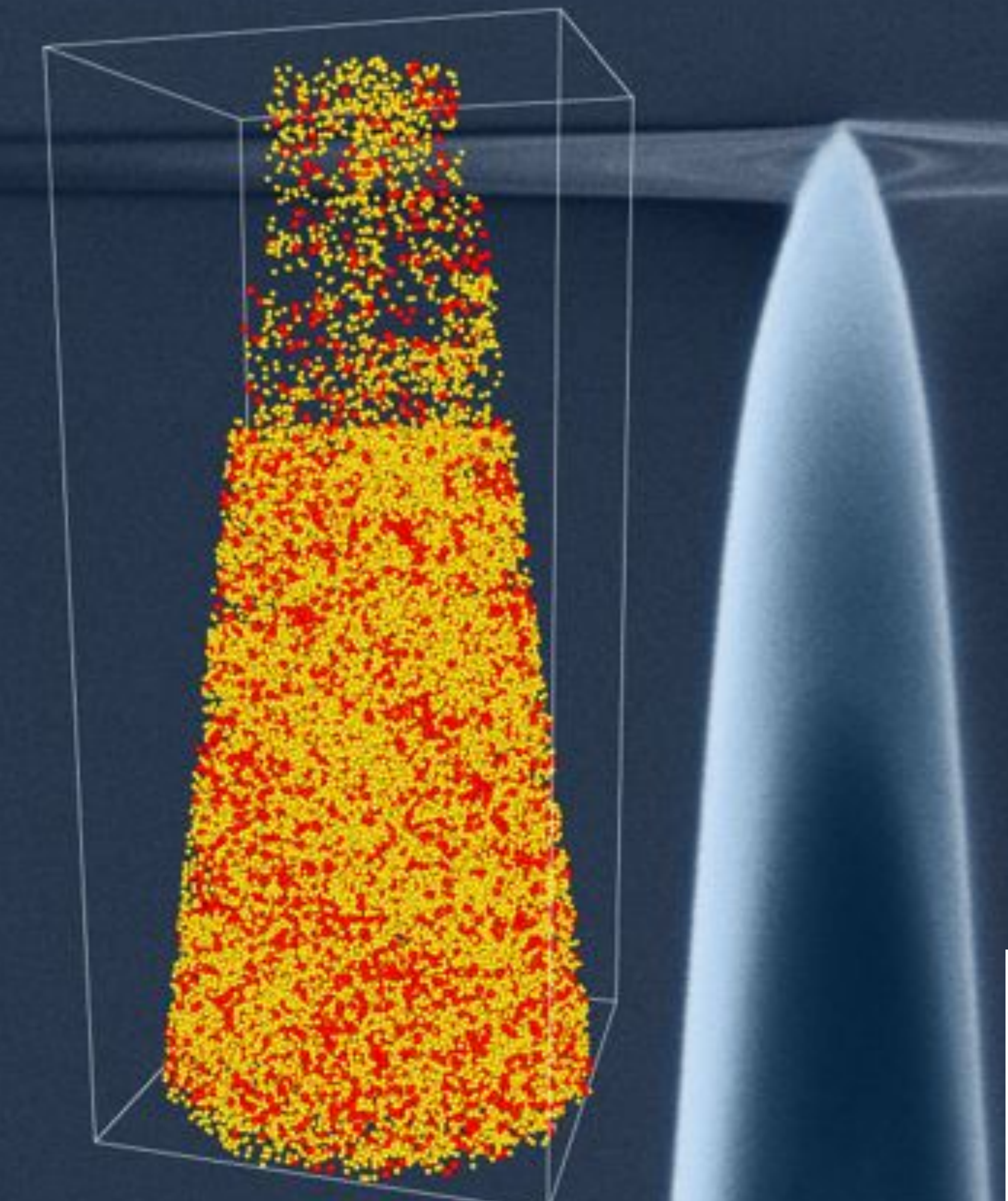
(low *Z*)



Atom probe tomography: mass (isotope) spectra

(higher *Z*)





3-dimensional reconstruction
of altered 1-month glass
by APT

red = boron
yellow = calcium

nature materials

LETTERS

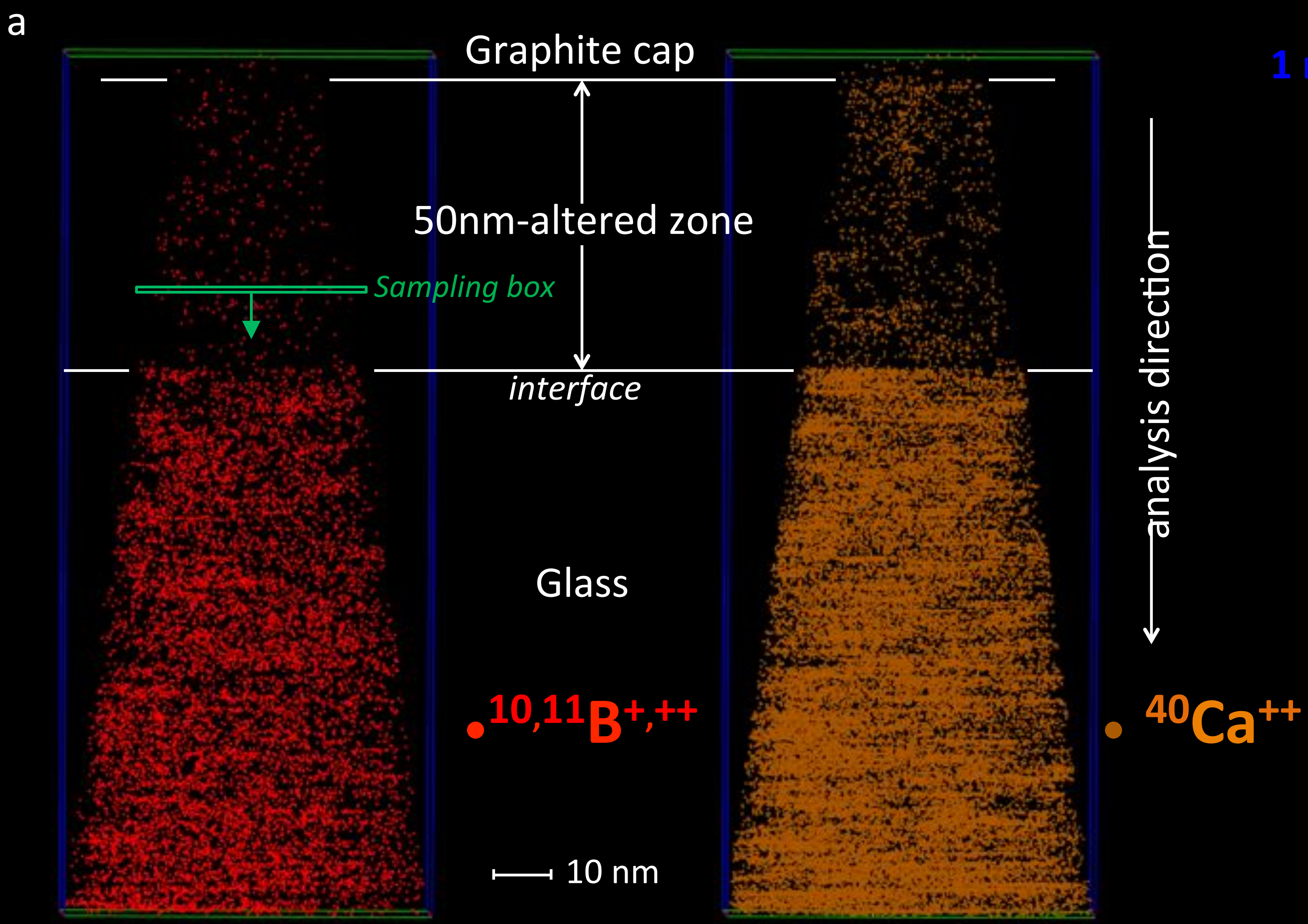
PUBLISHED ONLINE: 5 JANUARY 2015 | DOI: 10.1038/NMAT4172

Nanometre-scale evidence for interfacial dissolution–reprecipitation control of silicate glass corrosion

Roland Hellmann[1,2]*, Stéphane Cotte[1,2†], Emmanuel Cadel[3], Sairam Malladi[4], Lisa S. Karlsson[5†],
Sergio Lozano-Perez[5], Martiane Cabié[6] and Antoine Seyeux[7]

APT: chemical maps of B and Ca

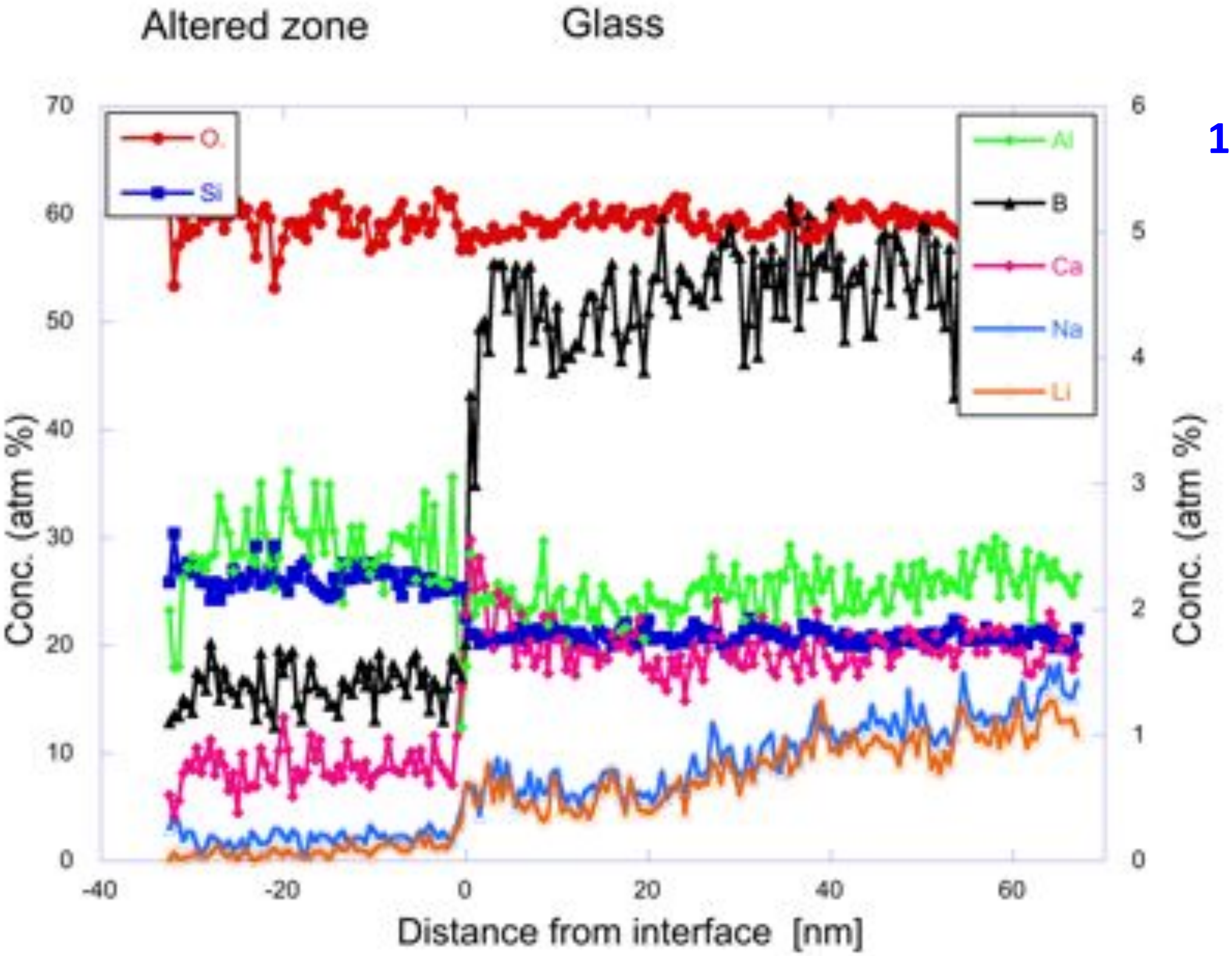
1 month



63.8 x 63.8 x 148.6 nm

Hellmann et al. 2015
Nature Materials

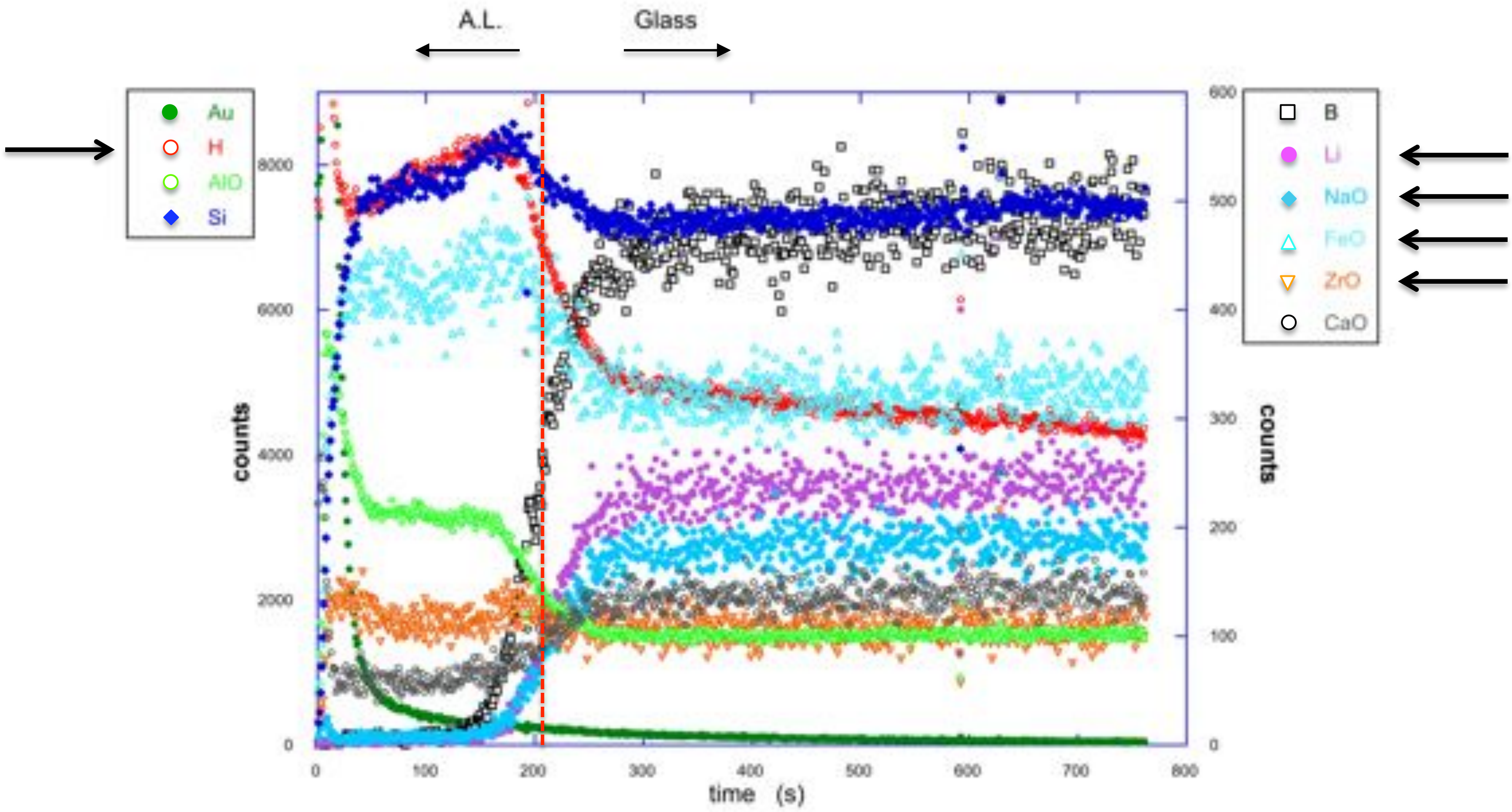
APT: chemical profiles



1 month

ToF-SIMS: complementary chemical profiles

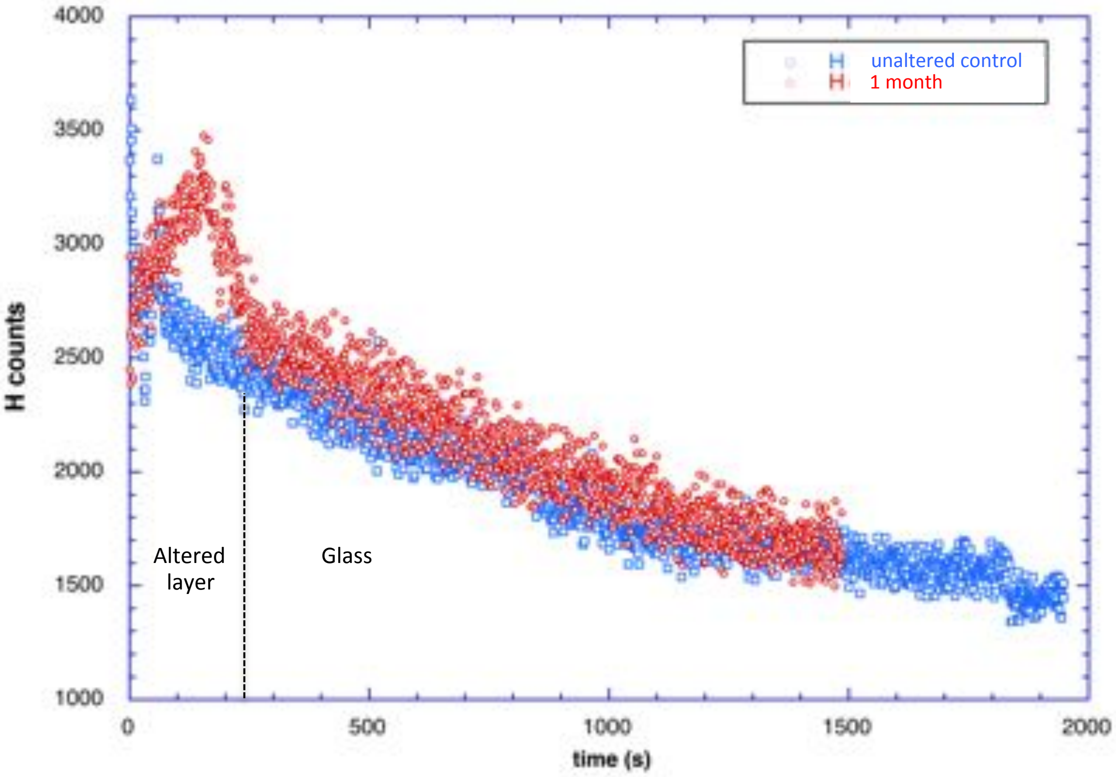
1 month



note that poor spatial resolution of ToF-SIMS analyses artificially broadens gradients

ToF-SIMS: complementary H profiles

1 month



note high degree of hydration of surface altered layer

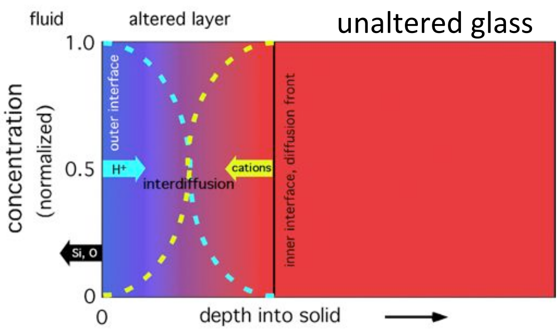
interdiffusion modeling

can nm-sharp chemical gradients
(lab and nature)
be explained by diffusion?
(i.e. leached layer formation)

specific case: 400-nm thick altered layer

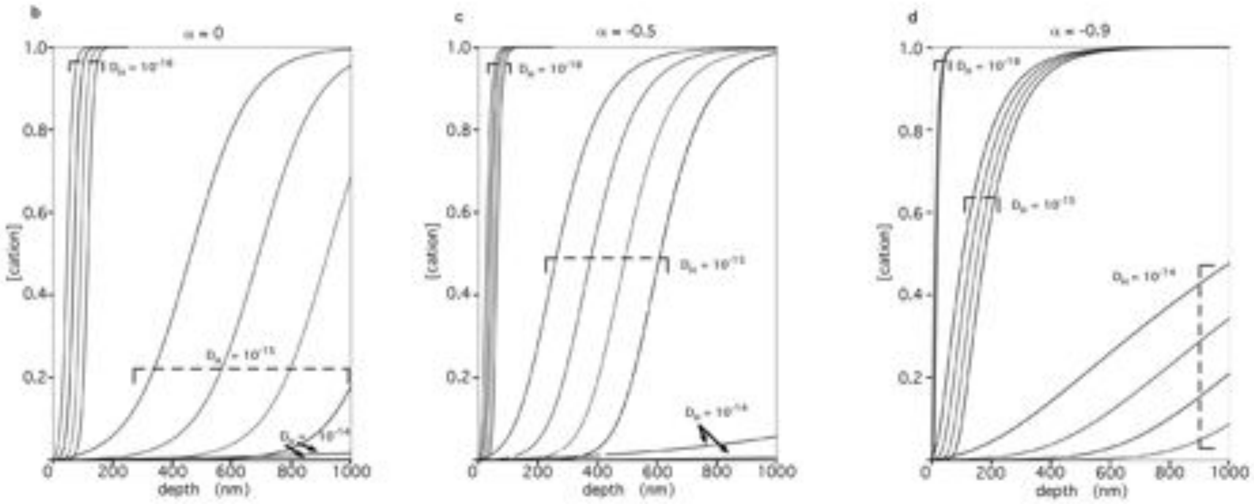
standard interdiffusion expression with moving boundary:

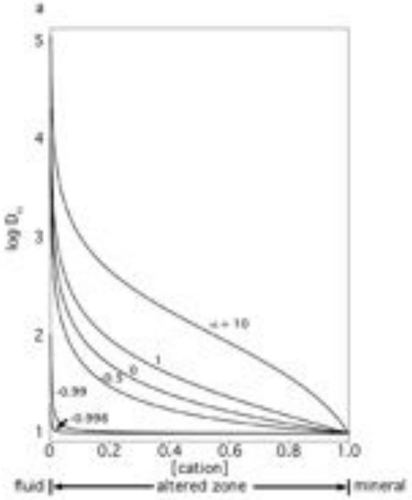
$$\frac{\partial C_{\mathrm{H}}}{\partial t} = \frac{\partial}{\partial x}\left(D^{*}\frac{\partial C_{\mathrm{H}}}{\partial x}\right) + a\frac{\partial C_{\mathrm{H}}}{\partial x} = 0$$



- **binary interdiffusion of protons and cations,**
- **solid state volume diffusion**
- **semi-infinite geometry, [C] is constant at fluid-solid interface**
- **planar, non-stationary (*i.e.* retreating) fluid-solid interface**
- **C_{H} = normalized conc. of diffusing species H^{+}, $C_{\mathrm{H}} = 1 - C_{\mathrm{cation}}$**
- **D^{*} = interdiffusion coefficient**
- **x is the depth into the altered layer (from fluid-solid interface)**
- **a = rate of retreat of the fluid-solid (outer) interface (Si release)**
- $\partial C / \partial t = 0$ **assumes steady-state**

standard interdiffusion expression with moving boundary:

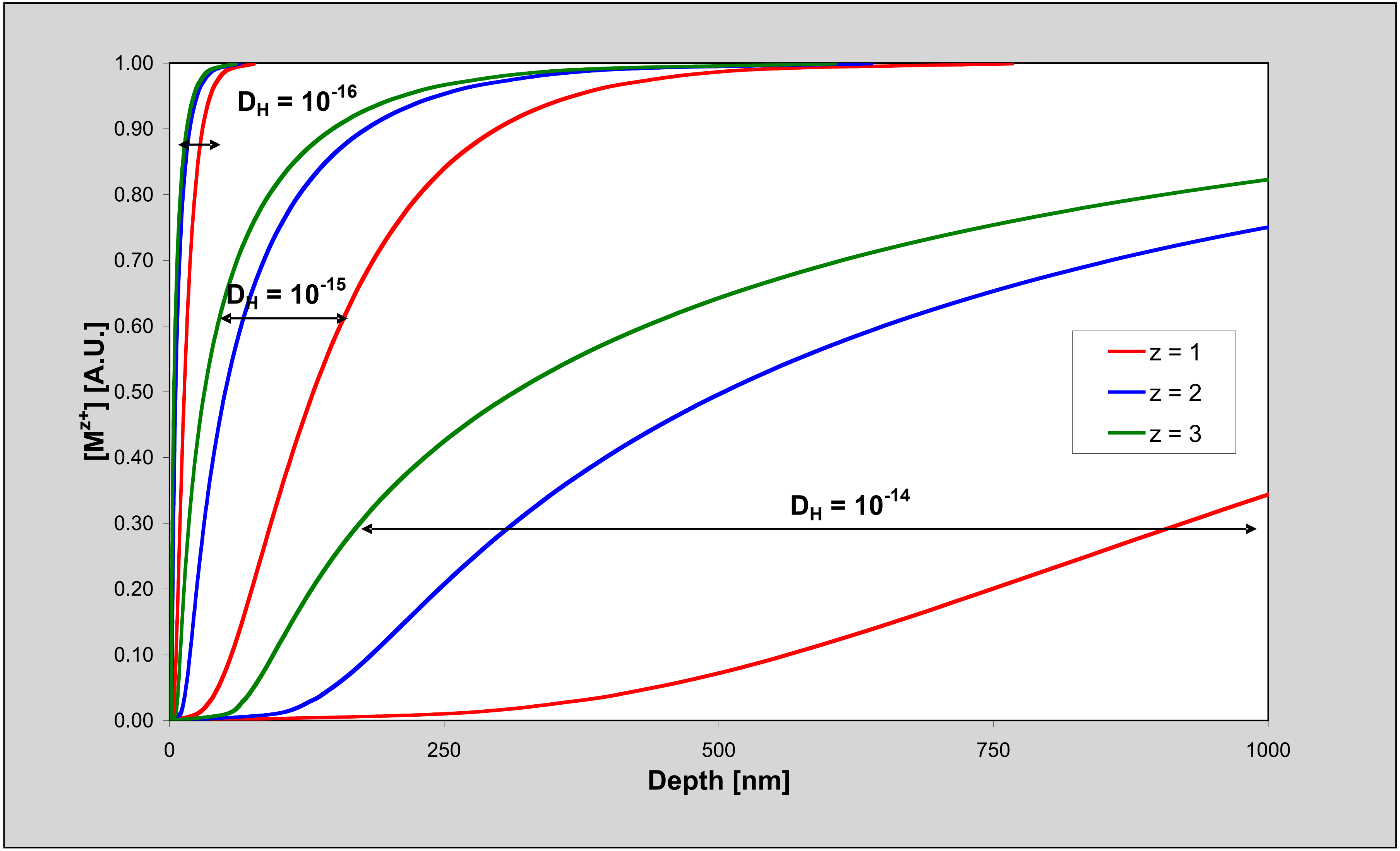




$$D_\alpha = (1 + \alpha C_{\mathrm{H}}) D^*$$

variables tested:

α, D_H, D_H / D_{cation} (= 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5})



D_H (H$^+$ diffusion coefficient cm^{2}s^{-1}), $D_H / D_{cation} = 10^{-3}$
cation valence (z), $a = 10^{-2}$ Å s^{-1}

can nm-sharp chemical gradients be explained by interdiffusion? (i.e. leached layer formation)

answer: most probably not

1. **cannot reproduce sharp chemical gradients (for altered layer thickness > 50 nm)**
2. **EFTEM/APT/ToF-SIMS results show no dependence of gradient on valence of cation**
3. **at 25 °C, solid-state diffusion is simply too slow!**
4. **cannot explain switch in chemistry of altered surface layers with pH**

news & views

GLASS CORROSION

Sharpened interface

The finding of a sharp interface between a chemically attacked surface and the pristine bulk in a borosilicate glass is at odds with the widely held diffusion-based mechanisms of glass durability.

Andrew Putnis

Corrosion of glasses: a break with the status quo mechanism

The need to find an alternative explanation to preferential leaching and interdiffusion has led to the idea of applying *coupled interfacial dissolution-reprecipitation* (CIDR)

Traditional corrosion/weathering mechanism: solid-state volume interdiffusion/preferential leaching

Evidence against:

Glass/mineral-altered zone interface: extremely sharp,

  spatially coincident structural + chemical changes

  interdiffusion: smooth sigmoidal chemical profiles

Depths of cation depletion: always equal, independent of cation charge, +1 to +4;

  but, interdiffusion distance inversely proportional to cation charge

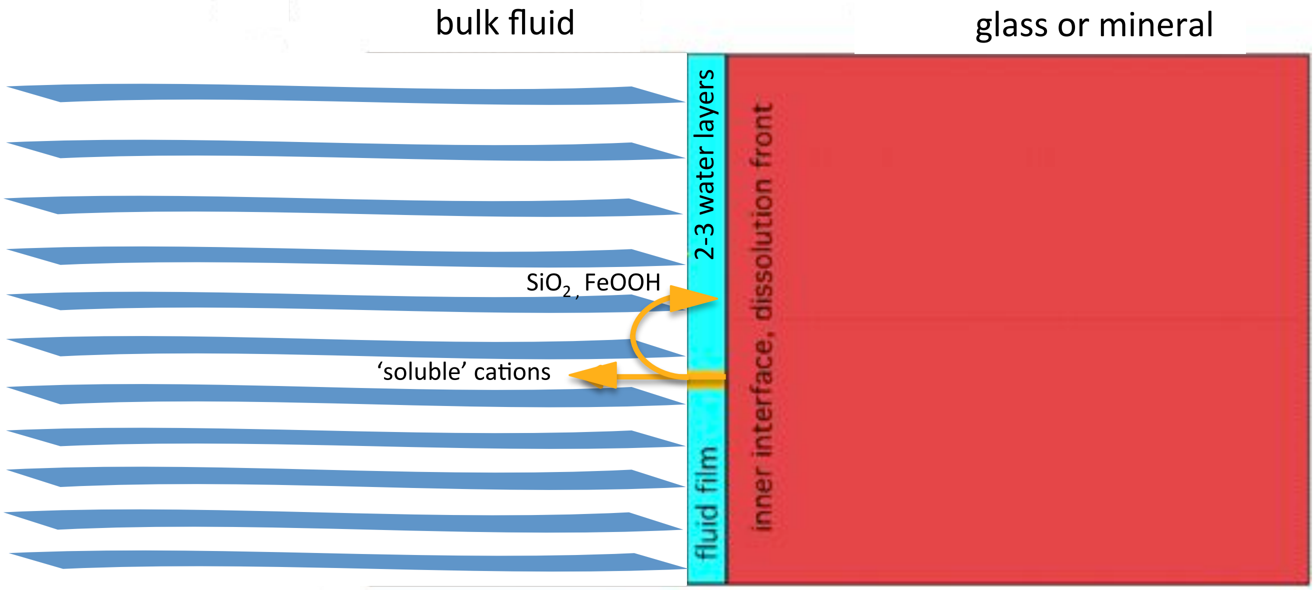
Interdiffusion cannot result in element enrichment (Si, Al, Fe)

Evidence of structural detachment at interface (both glasses & minerals)

Rates of solid-state interdiffusion: far too slow at low *T*

Interdiffusion depends on H^+-cation exchange: incompatible with basic pH corrosion

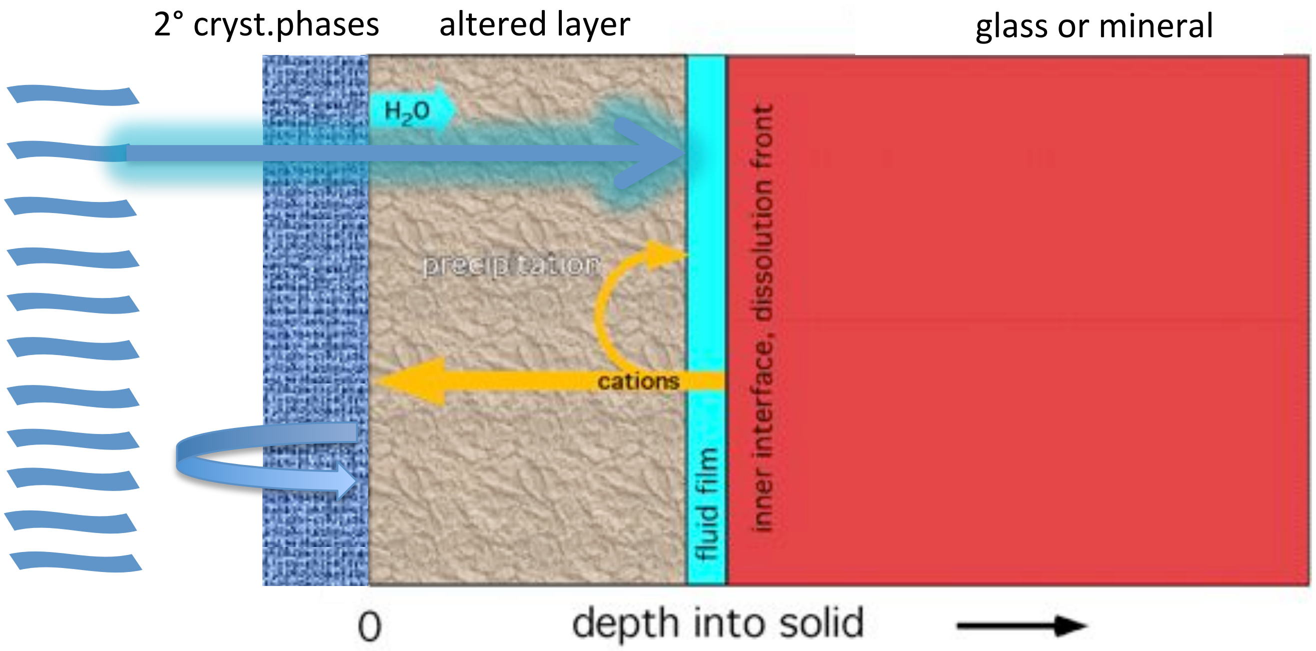
A new* mechanism of chemical weathering & corrosion: coupled interfacial dissolution reprecipitation (CIDR)



*O'Neil & Taylor, 1967: feldspar-feldspar replacement

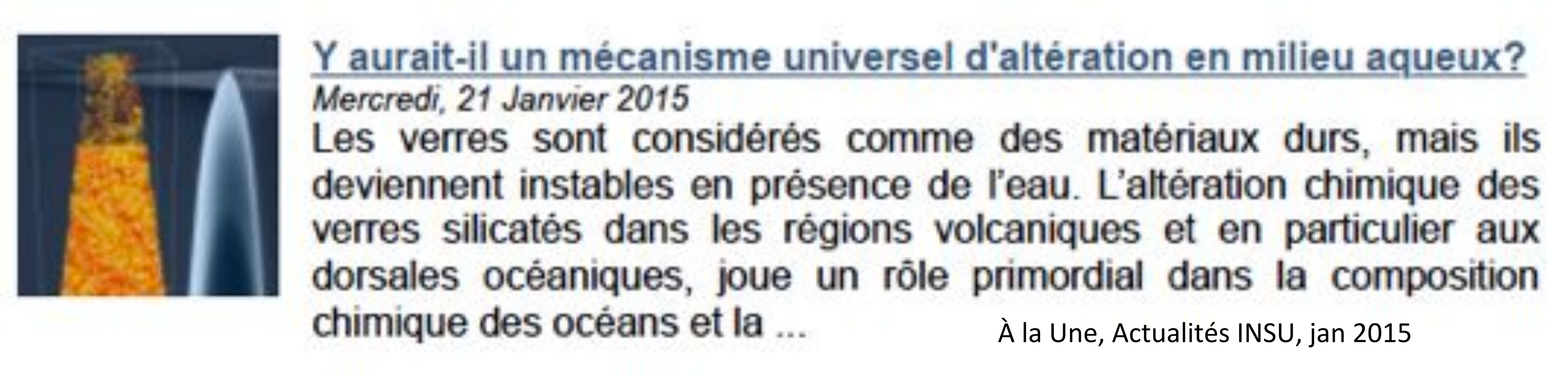
1. a <u>thin interfacial fluid film</u> is present at pristine phase interface; its physical, chemical, rheological properties (dielectric constant, structure, diffusion, H-bonding) are much different than bulk fluid
2. local chemical disequilibrium: <u>chemical hydrolysis</u> reactions lead to advance of reaction front into 1° phase (all bonds are broken, no relict structure formed); NO interdiffusion-control
3. dissolution leads to *interfacial* supersaturation, coupled in space and time to precipitation: hydrated silica gel + other insoluble cation oxyhydroxides (Fe, Al, Zr, Mo)
4. 'soluble' cations released into bulk fluid (Li, Na, K, Ca, Mg, etc.)

A new mechanism of chemical weathering & corrosion: coupled interfacial dissolution reprecipitation



4. intrinsic dissolution process (*i.e.* at interface of unaltered phase) is stoichiometric at all pH conditions (no pH-dependent preferential removal of cations)
5. net volume deficit for overall reaction = precipitated 2° altered layer is porous/permeable
6. bulk solution oversaturation can lead to precipitation of SiO_2, crystalline 2° phases at outer surface
7. 2° phase porosity can potentially evolve, leading to passivation of kinetics at inner interface

What's next ?



Y aurait-il un mécanisme universel d'altération en milieu aqueux?

Mercredi, 21 Janvier 2015

Les verres sont considérés comme des matériaux durs, mais ils deviennent instables en présence de l'eau. L'altération chimique des verres silicatés dans les régions volcaniques et en particulier aux dorsales océaniques, joue un rôle primordial dans la composition chimique des océans et la ...

À la Une, Actualités INSU, jan 2015

Collaborations and support from:

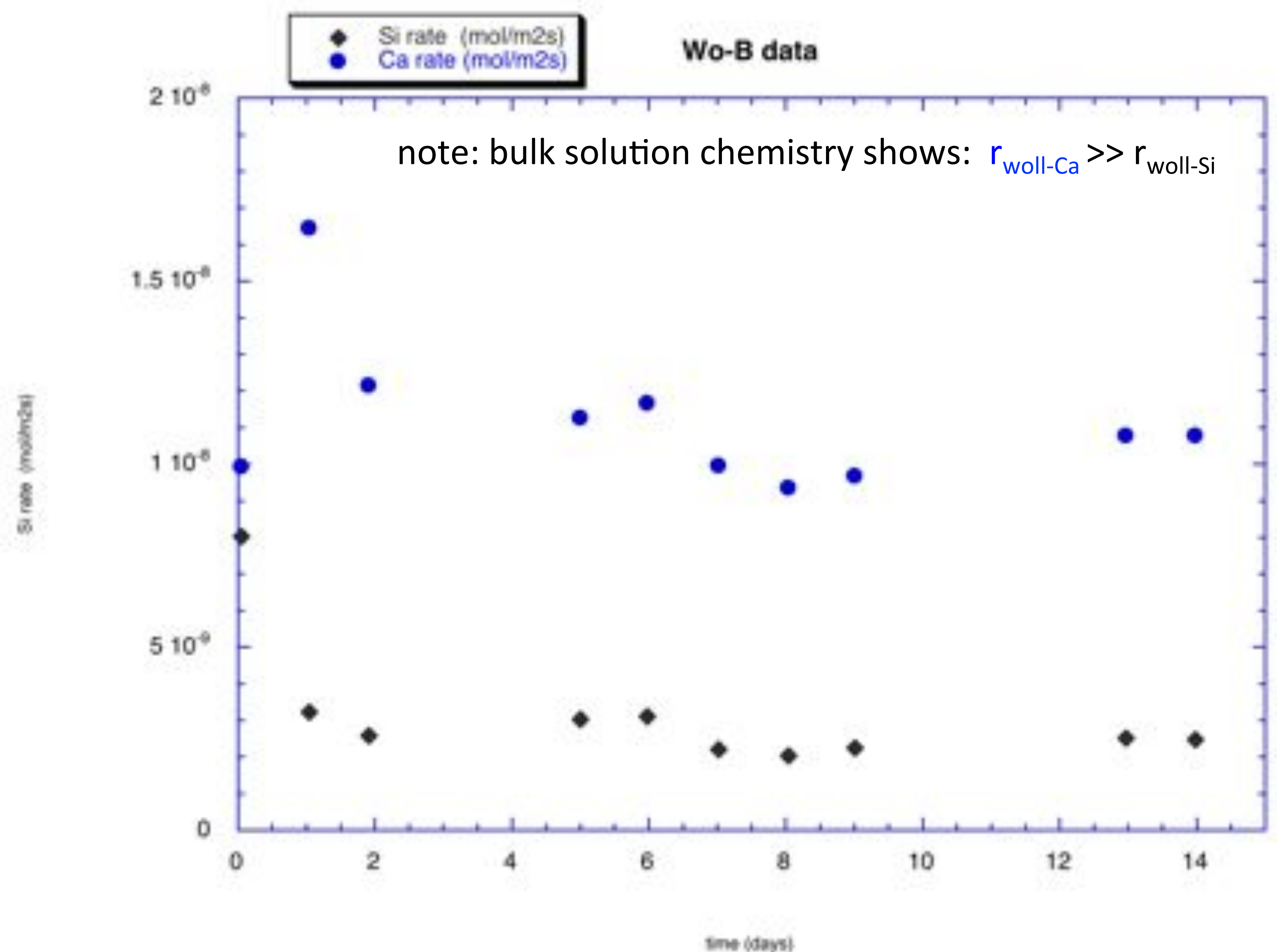
Antoine Seyeux, Emmanuel Cadel, Sairam Malladi, Lisa Karlsson, S. Lozano-Perez, Martiane Cabié, S. Cotte, C. Vollmer, D. Daval, O. Stéphane, J. Neeway, A. Abdelouas, CEA-Marcoule

Financial support: METSA & ESTEEM1, 2; ANDRA

Belledonne Massif, Grenoble

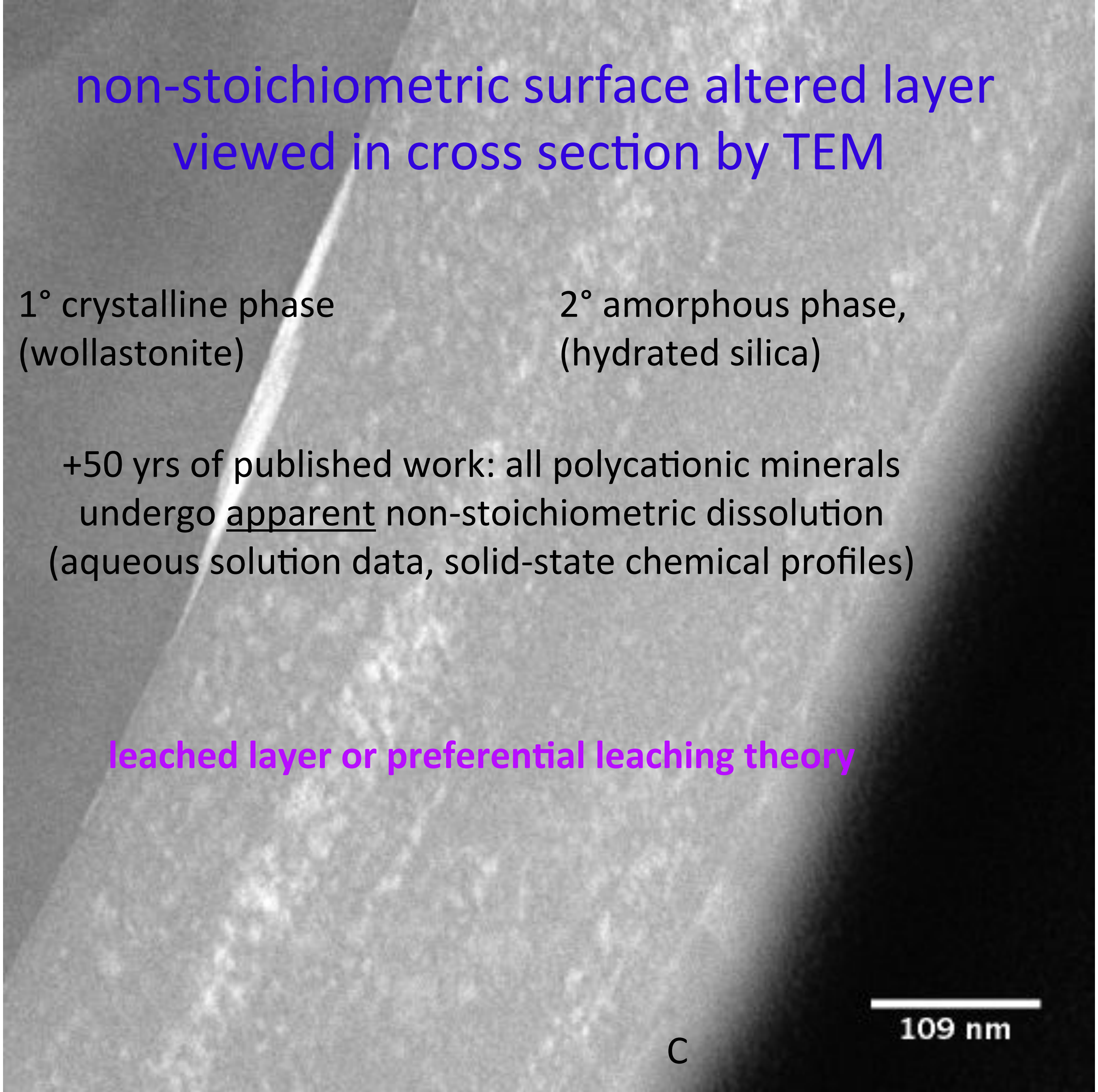
Apparent non-stoichiometric dissolution: formation of so-called 'leached layer'

aqueous data for wollastonite dissolution, pH 3, 25 °C



note: bulk solution chemistry shows: $r_{woll\text{-}Ca} >> r_{woll\text{-}Si}$

non-stoichiometric surface altered layer viewed in cross section by TEM



1° crystalline phase
(wollastonite)

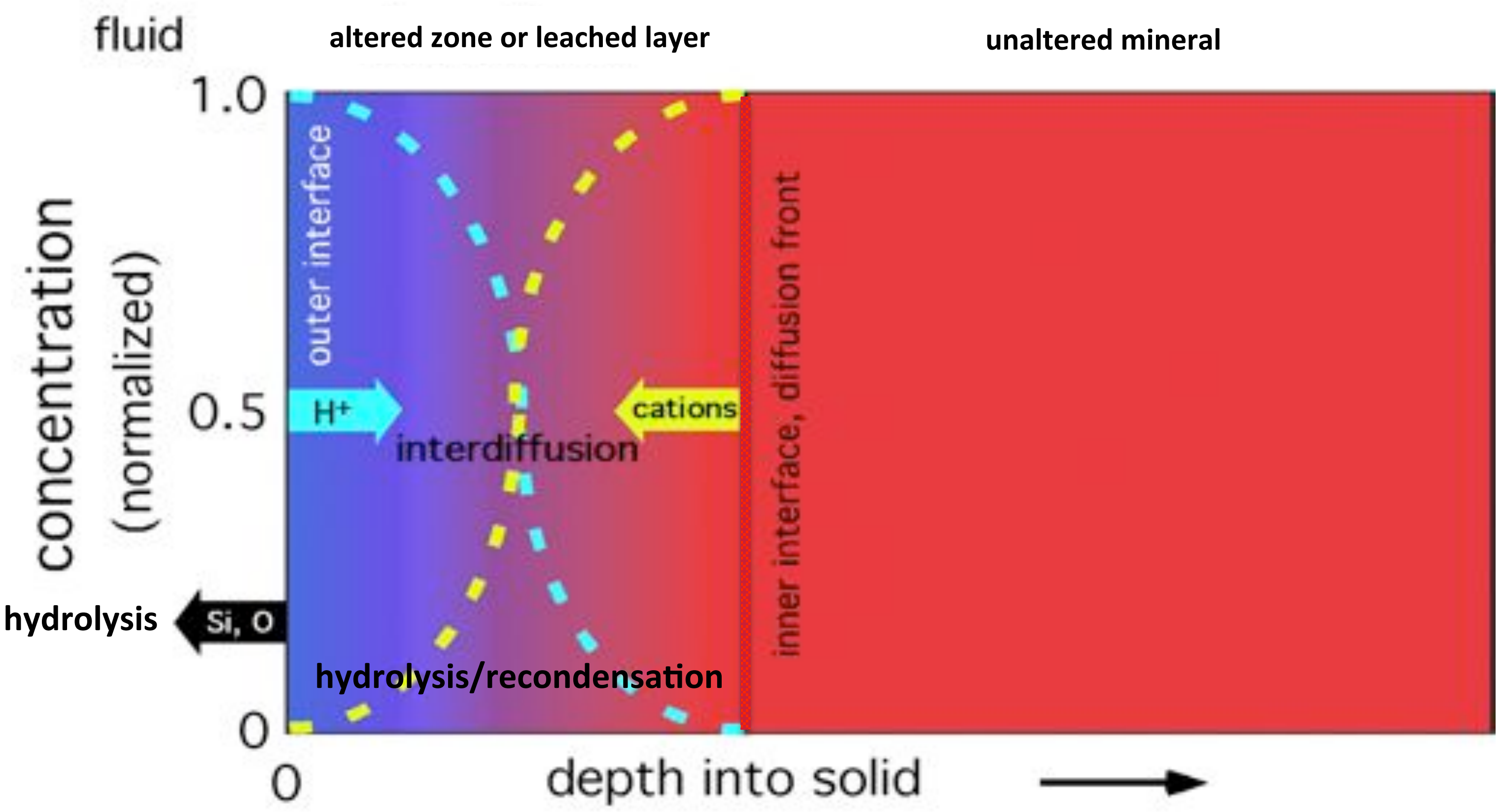
2° amorphous phase,
(hydrated silica)

+50 yrs of published work: all polycationic minerals undergo apparent non-stoichiometric dissolution (aqueous solution data, solid-state chemical profiles)

leached layer or preferential leaching theory

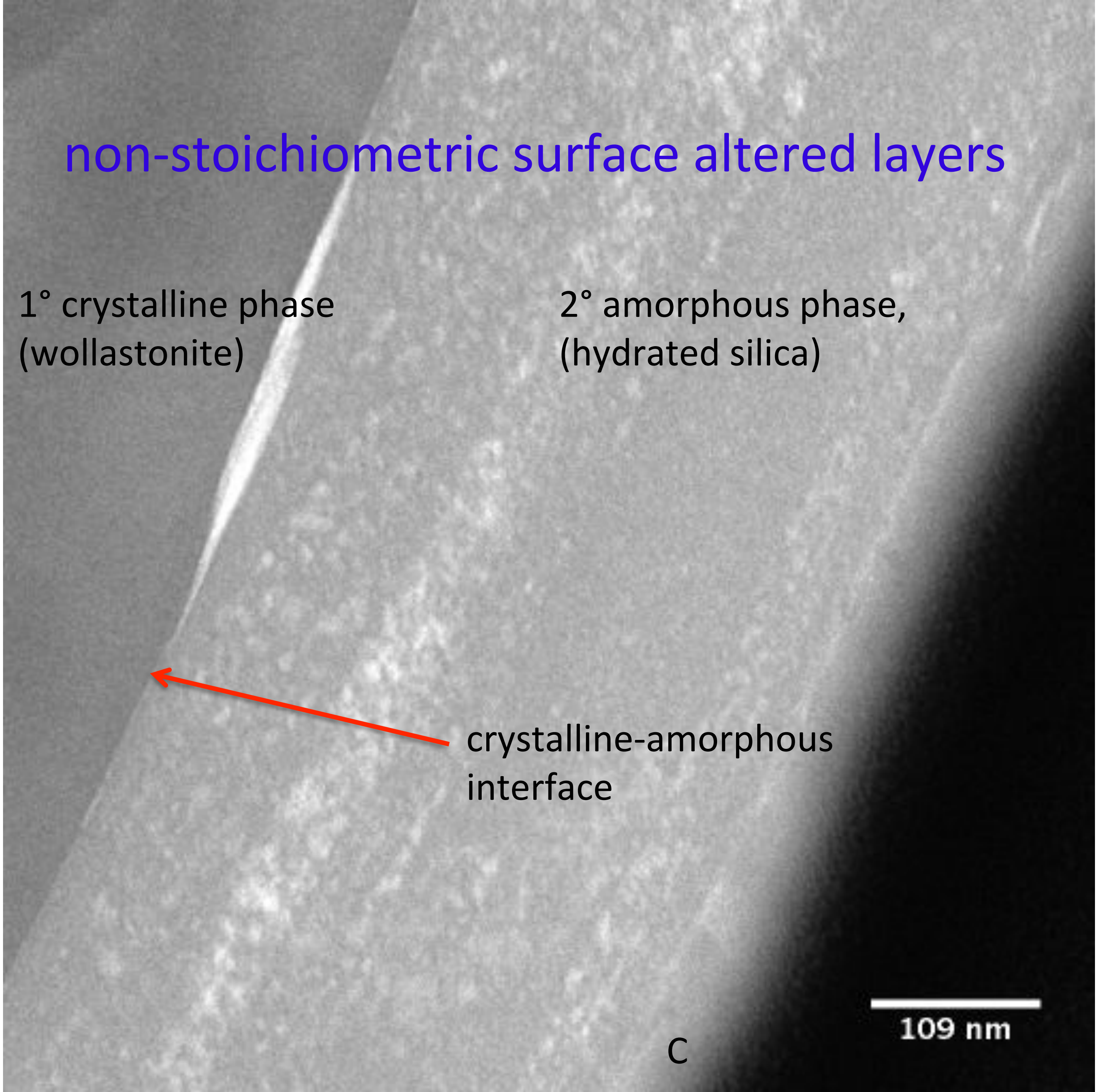
Wo-B

Current and traditional mechanism for chemical weathering of minerals: leached layer model



in situ transformation via selective cation removal/exchange controlled by solid-state interdiffusion with H^+;
leached layer = covalently bonded, relict structure of 1° mineral

non-stoichiometric surface altered layers



1° crystalline phase
(wollastonite)

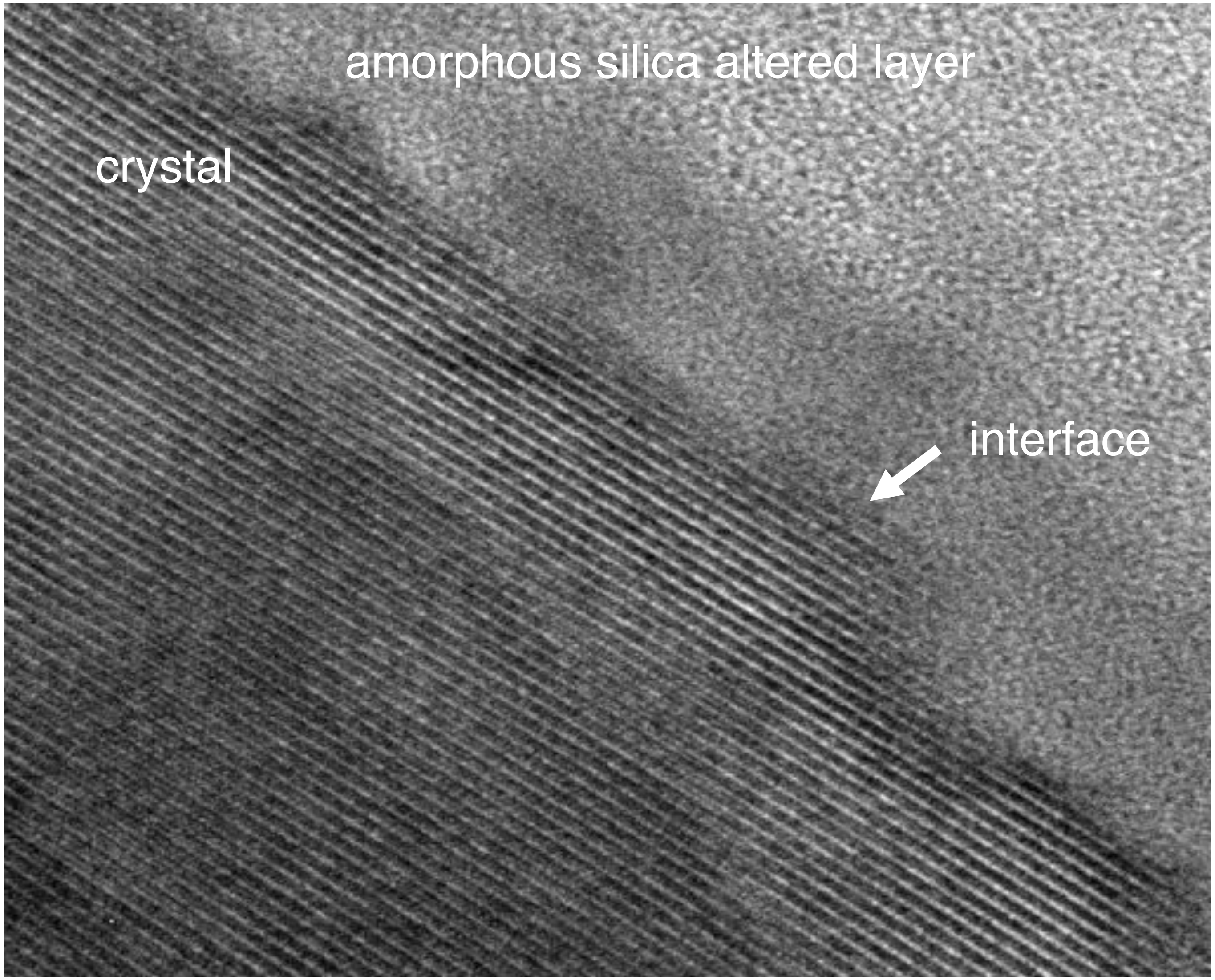
2° amorphous phase,
(hydrated silica)

crystalline-amorphous
interface

Wo-B

Mineral – amorphous surface altered layer

structural interface



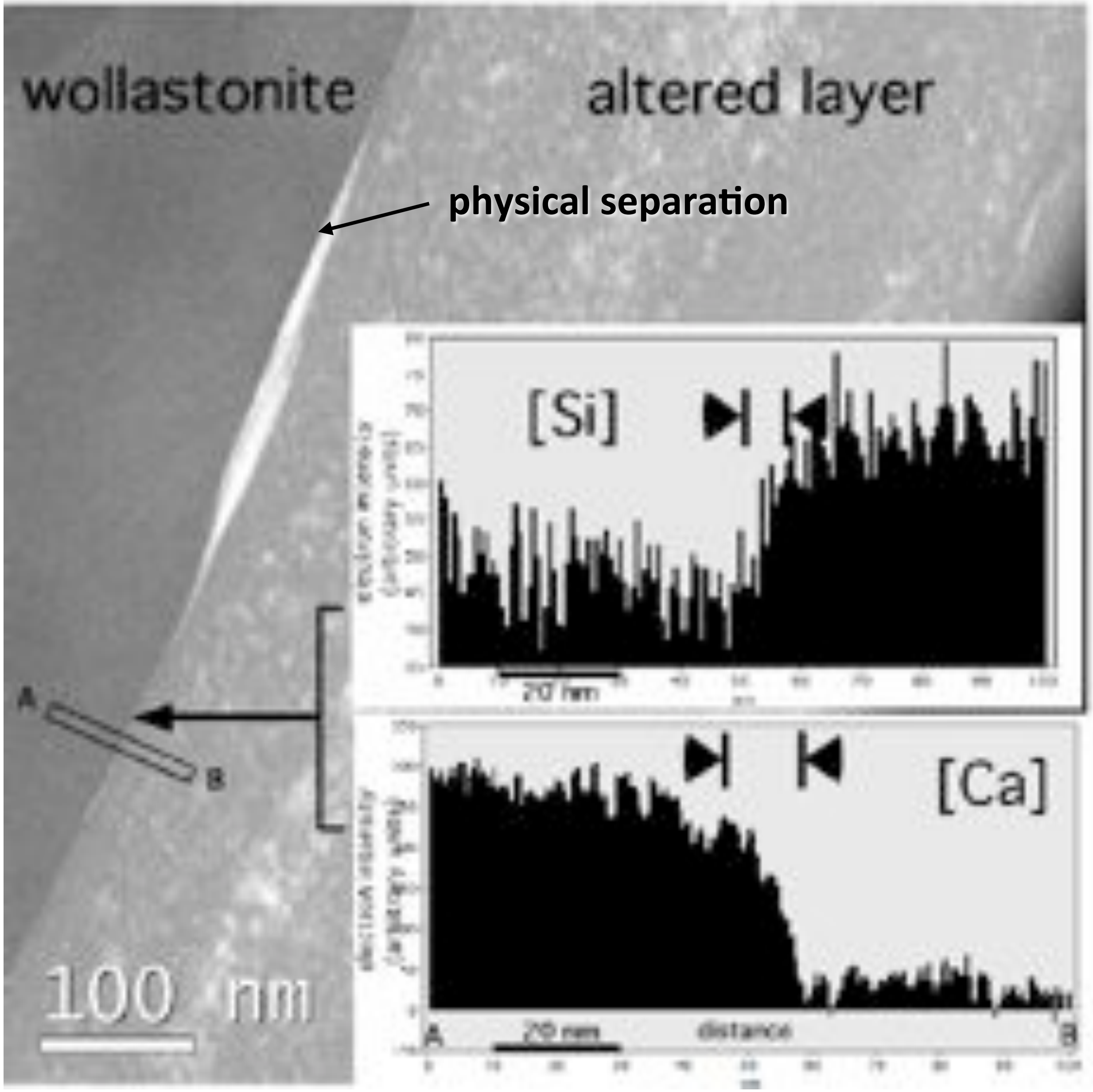
chain silicate:
wollastonite

pH 3, 25 °C
laboratory expt.

note: all Si phases
were undersaturated
in bulk fluid !

Mineral – amorphous surface altered layer

chemical interface



chain silicate:
wollastonite

pH 3, 25 °C

EFTEM profiles:
grad. widths = 6-12 nm

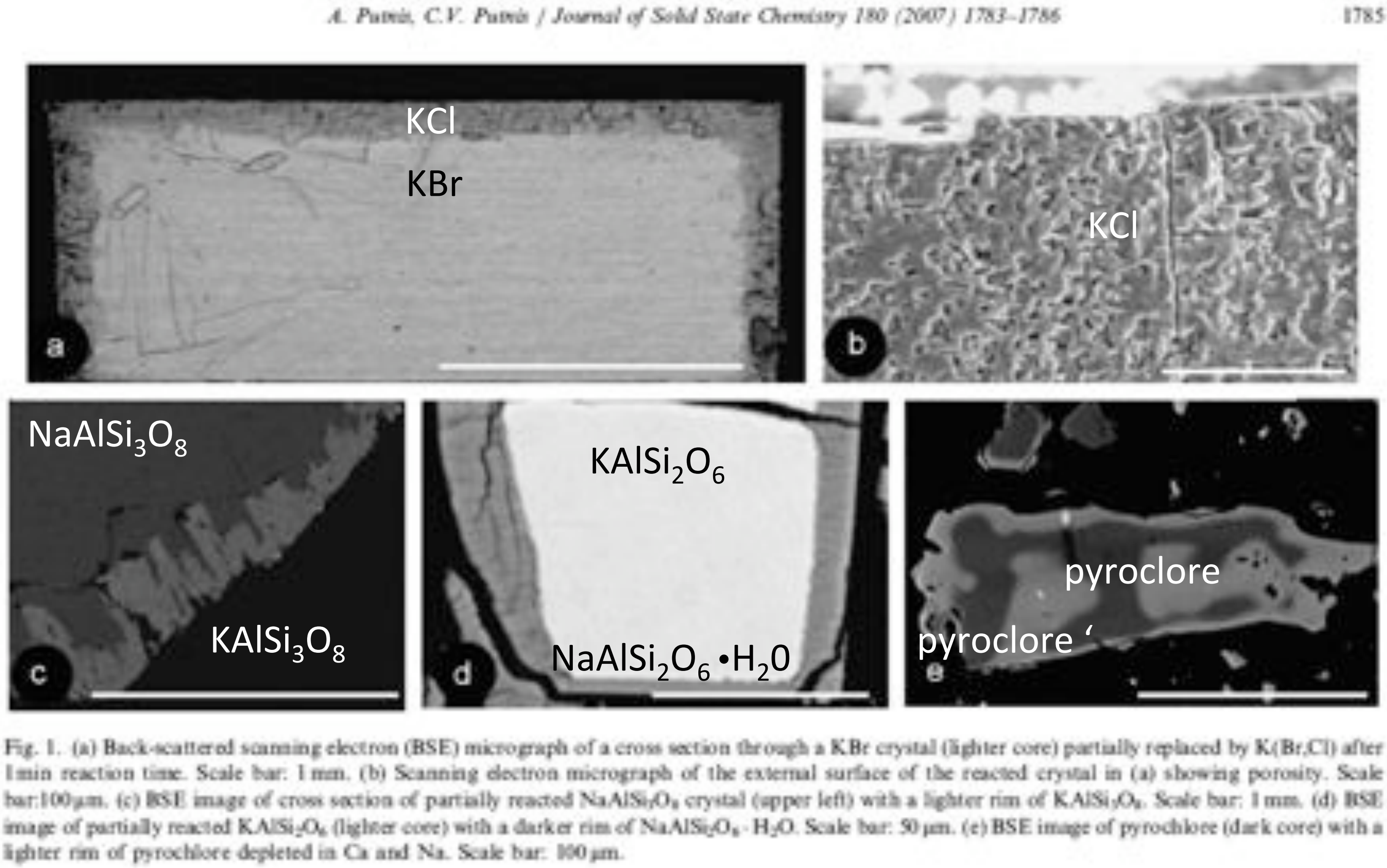
vs. 160 nm by SIMS !

note that abrupt changes in chemistry are spatially commensurate

Hellmann et al. 2012
Chemical Geology

Mineral-mineral replacement reactions

laboratory weathering: low to moderate temperatures

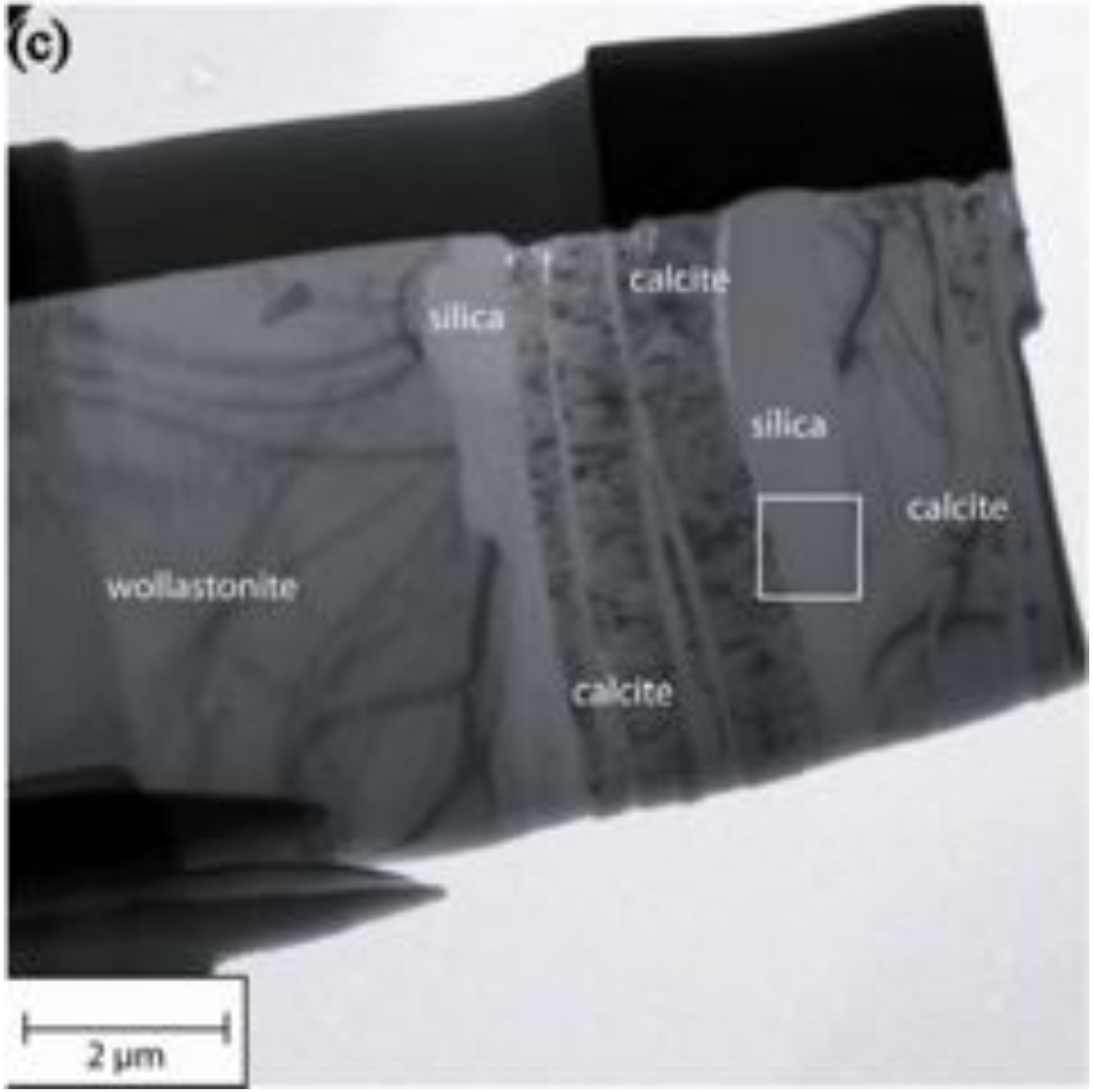


A. Putnis, C.V. Putnis / Journal of Solid State Chemistry 180 (2007) 1783–1786 1785

Fig. 1. (a) Back-scattered scanning electron (BSE) micrograph of a cross section through a KBr crystal (lighter core) partially replaced by K(Br,Cl) after 1 min reaction time. Scale bar: 1 mm. (b) Scanning electron micrograph of the external surface of the reacted crystal in (a) showing porosity. Scale bar: 100 μm. (c) BSE image of cross section of partially reacted NaAlSi$_3$O$_8$ crystal (upper left) with a lighter rim of KAlSi$_3$O$_8$. Scale bar: 1 mm. (d) BSE image of partially reacted KAlSi$_2$O$_6$ (lighter core) with a darker rim of NaAlSi$_2$O$_6$ · H$_2$O. Scale bar: 50 μm. (e) BSE image of pyrochlore (dark core) with a lighter rim of pyrochlore depleted in Ca and Na. Scale bar: 100 μm.

Mineral - surface altered layers: amorphous & crystalline

moderate temperatures, circum-neutral pH



wollastonite,

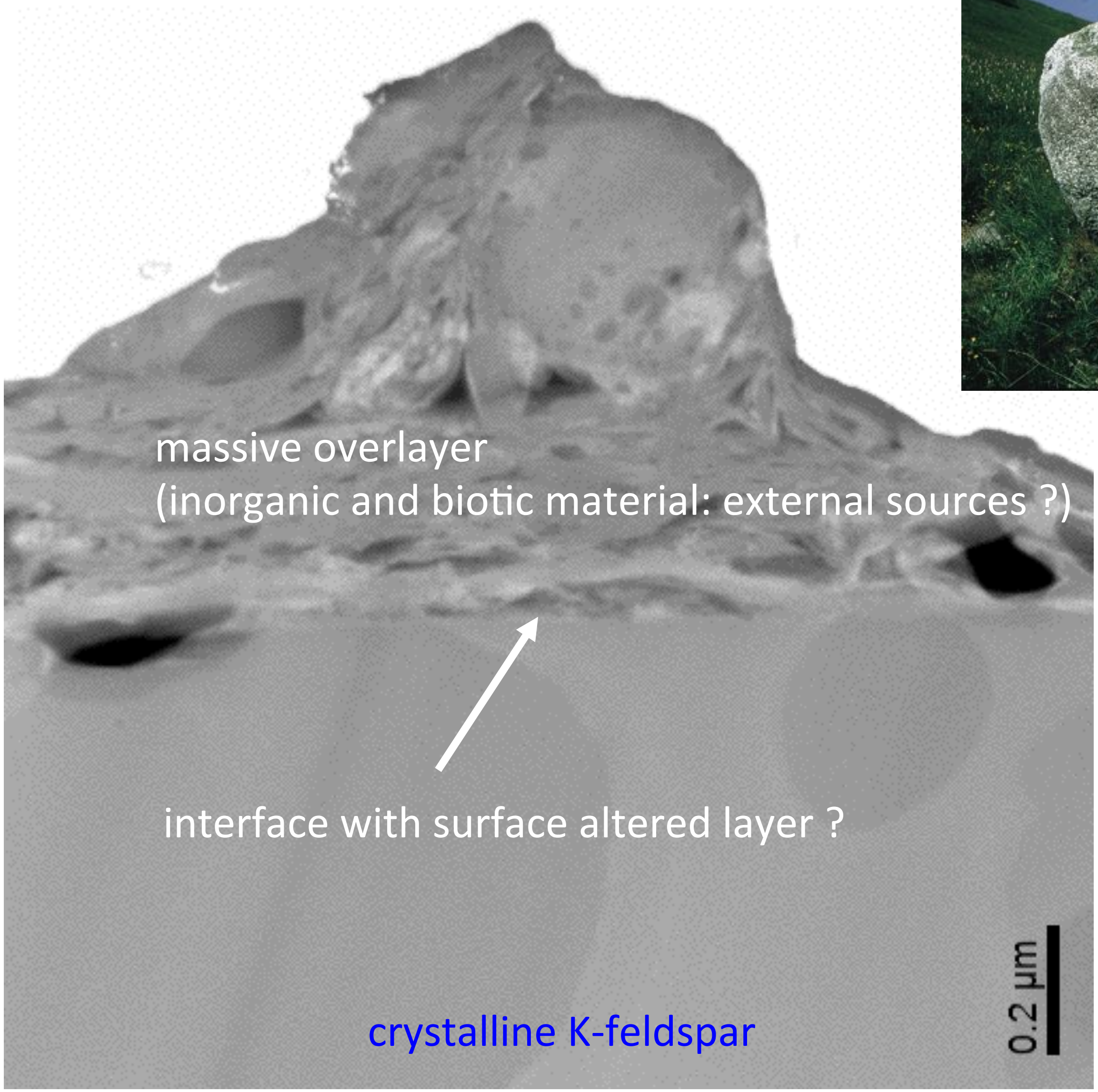
pH ≈ 3, 90 °C
$p\mathrm{CO}_2$ = 25 MPa

formation of thick, alternating surface layers of amorphous silica + (crystalline) calcite

from: Daval et al., 2009, *Amer. Miner.*

natural weathering: how does this occur?

(low temperatures, circum-neutral pH)



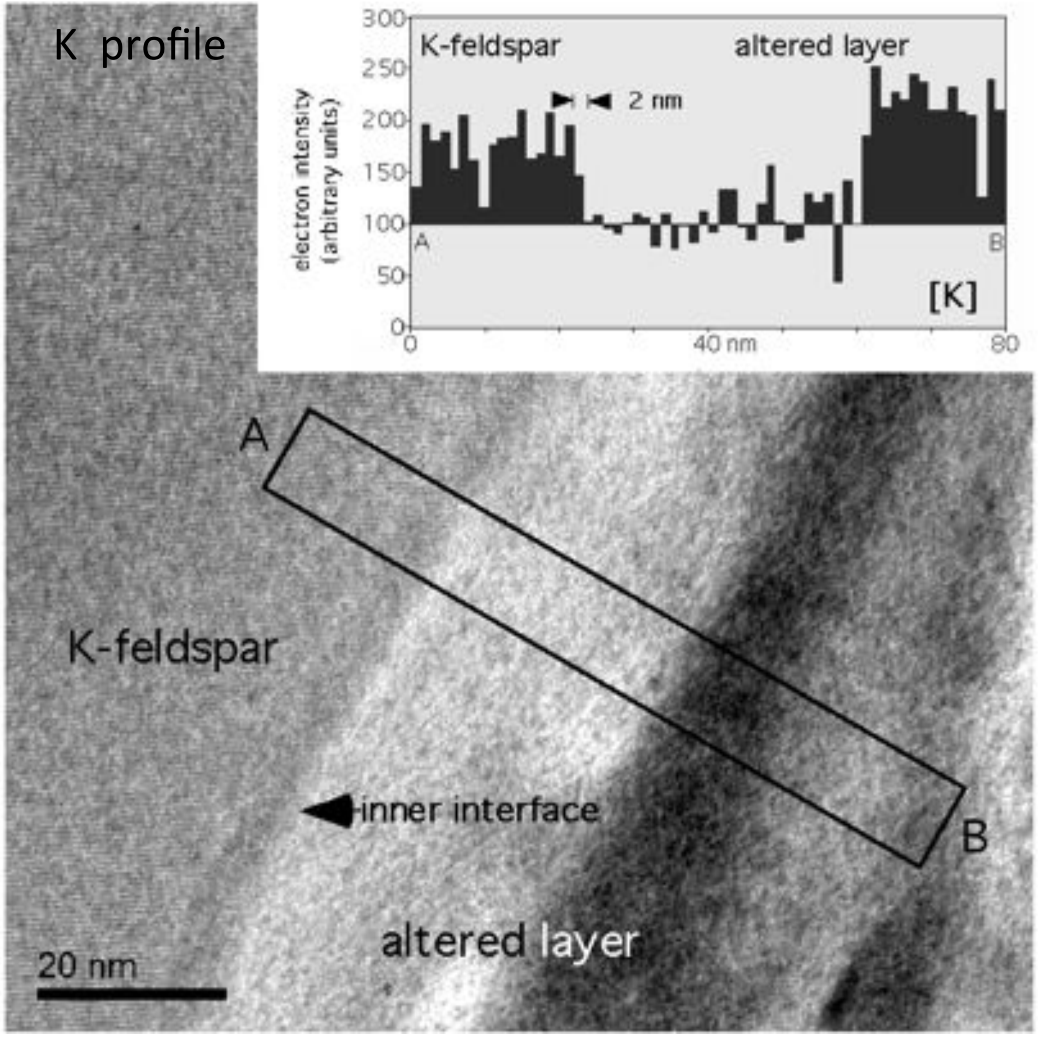
massive overlayer
(inorganic and biotic material: external sources ?)

interface with surface altered layer ?

crystalline K-feldspar

granitic erratic boulder
Pte. Andey, Hte. Savoie, France

natural weathering: surface altered layers also exist



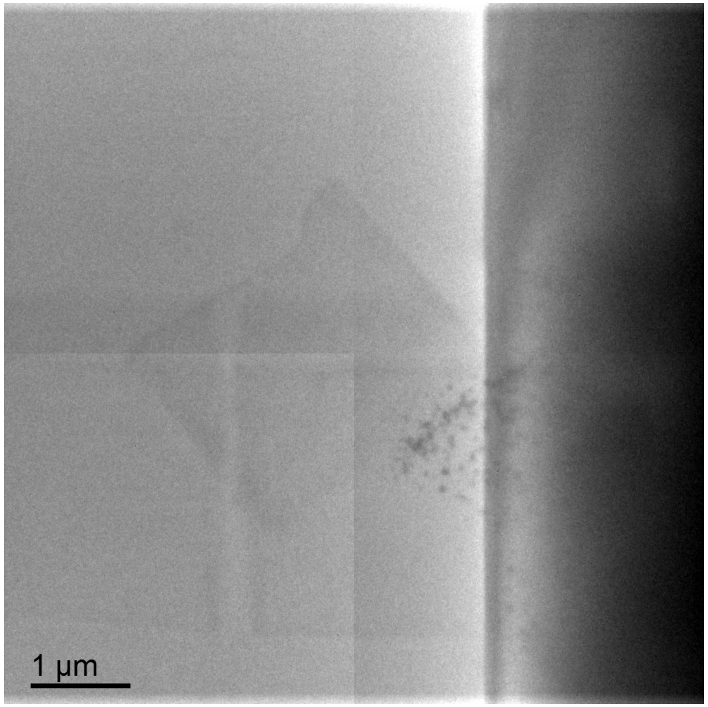
K profile

EFTEM profile

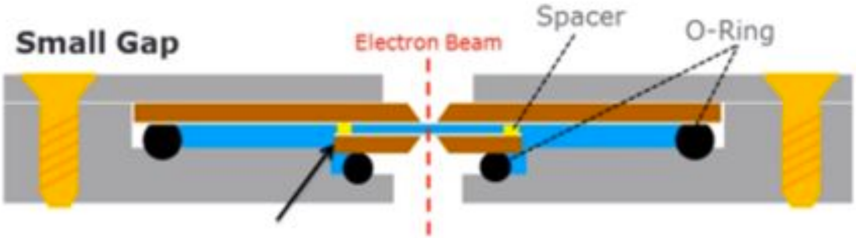
HRTEM

Measurement of fluid-solid interactions in situ and in real time at nm-scale resolution

Application of a 'frontier' analytical technique:
liquid cell TEM- to study chemical weathering in a native environment



wollastonite dissolution in situ



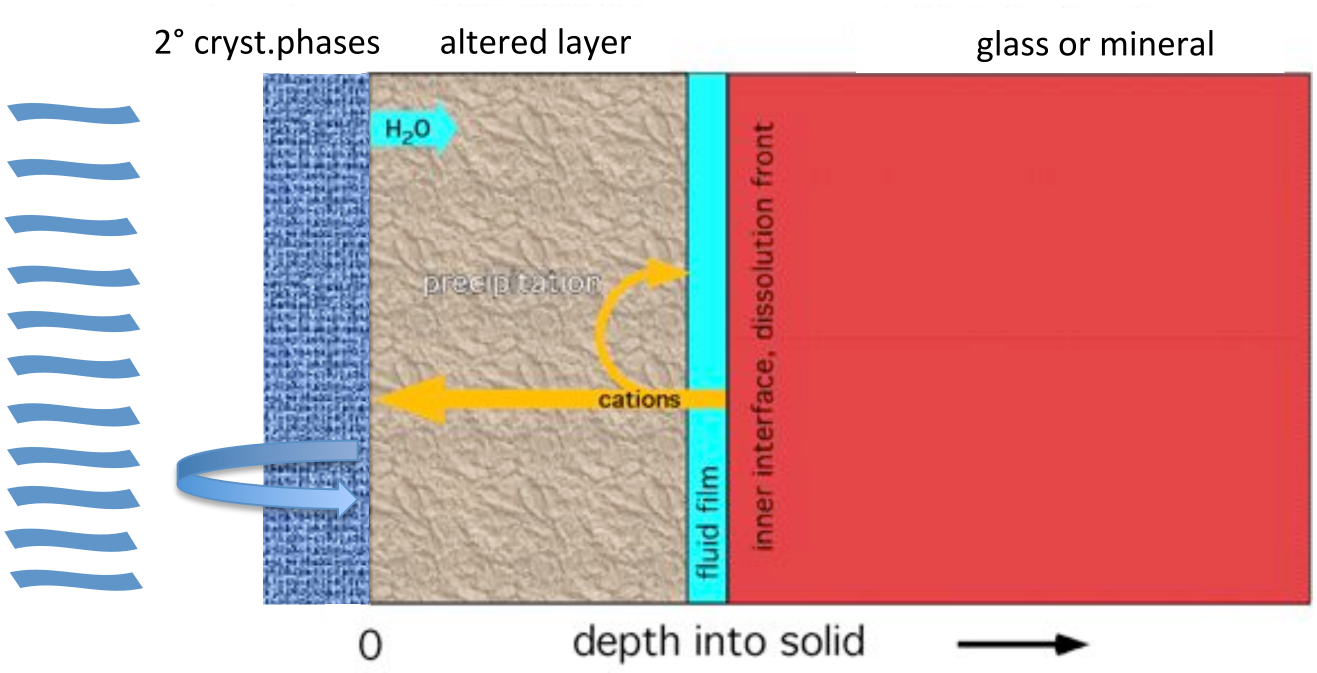
liquid cell TEM cutaway

Collaboration ISTerre (RH) - Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, TN, USA

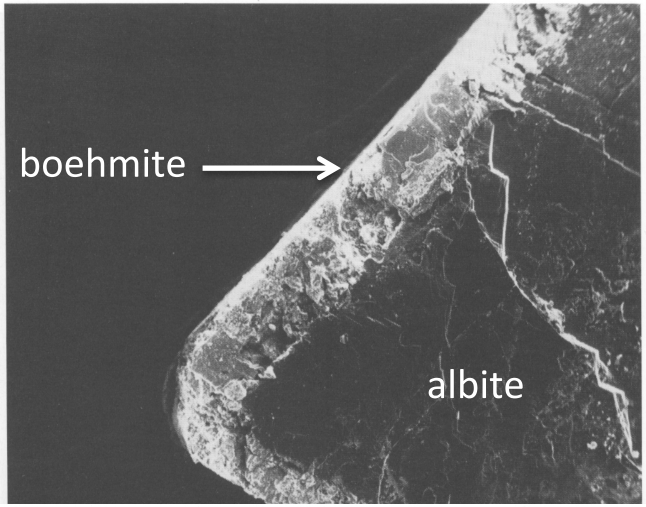
What is the difference between CIDR and ‘normal’ dissolution-precipitation ??

There must be evidence for a coupled interfacial process:

a. topotactic relation between 1° and 2° phase (up to 14% mismatch ok)
b. precipitation of 2° phase even though bulk fluid is undersaturated



Two 2° phases formed by CIDR?



from R. Hellmann et al., *Solid State Ionics*, 1989
(conditions: pH 2.4, 300 °C)

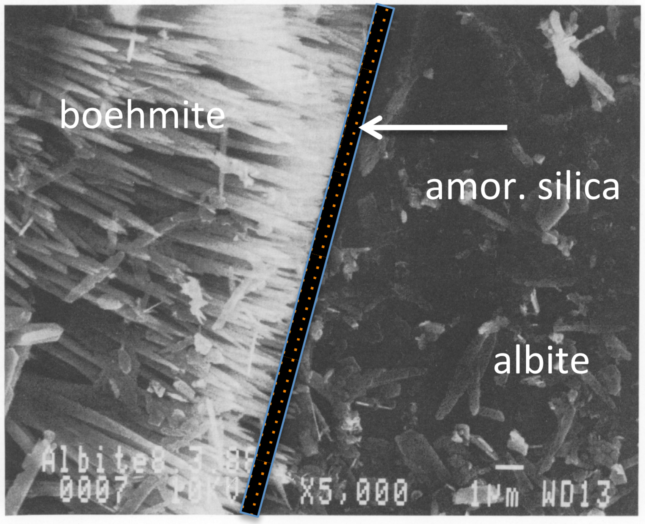


Fig. 10. A 5000× SEM image of the interface between boehmite and albite. Note how the tips of the boehmite crystals point in the direction of the interface, indicating possible growth in the direction of the retreating albite core.

Boehmite rind (0.5 mm): **NO**

precipitation due to bulk fluid oversaturation

Amorphous silica surface altered layer: **YES**

reprecipitation due to interfacial fluid supersaturation in contact with 1° phase

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