

# EPMA, Raman, and XANES applied for the study of oxidation processes in glass

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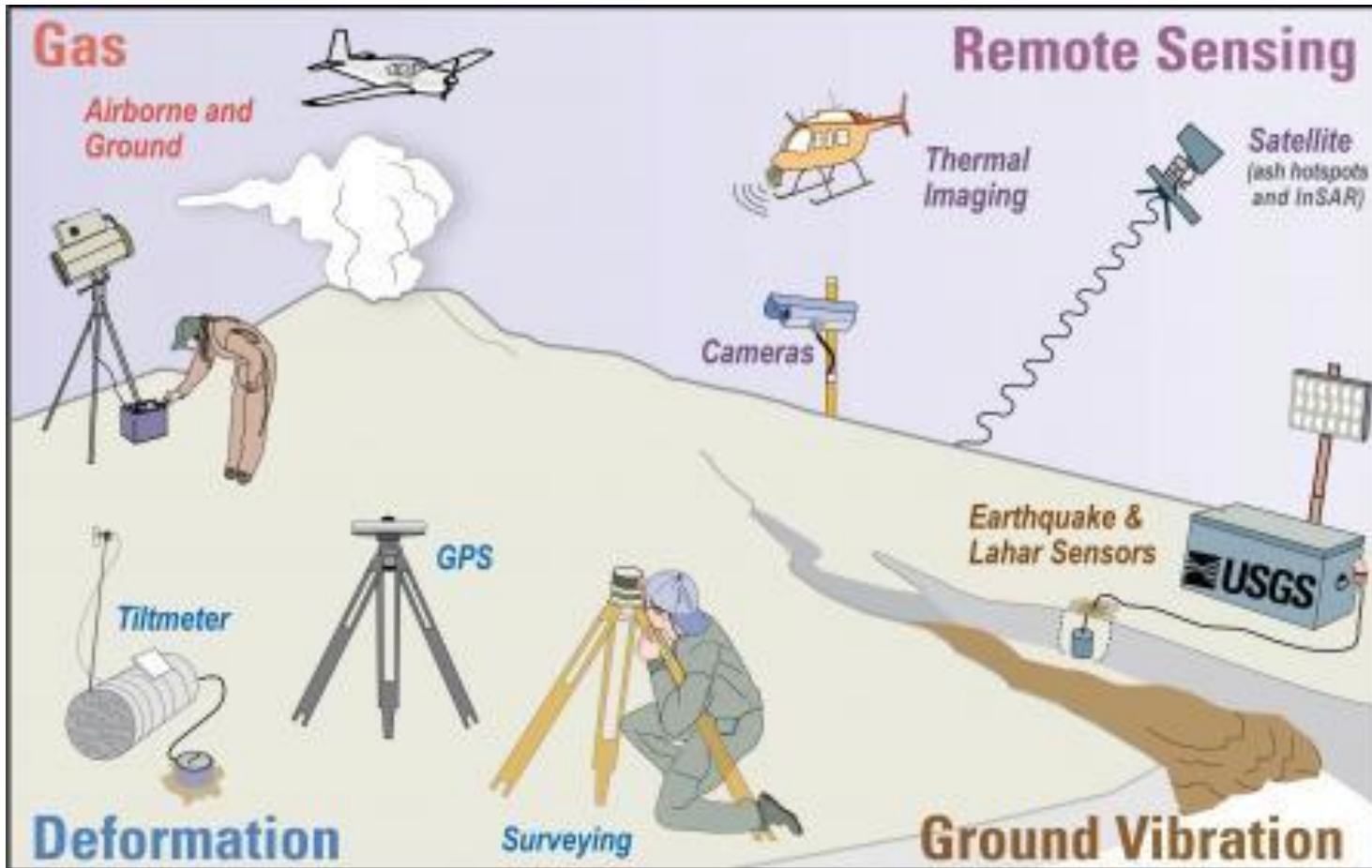
# What controls volcanic eruptions:

- Style
- Timing
- Location
- Duration



Volcán Osorno,  
Chile (E Hughes)

# Need to understand volcanic processes to interpret monitoring signals



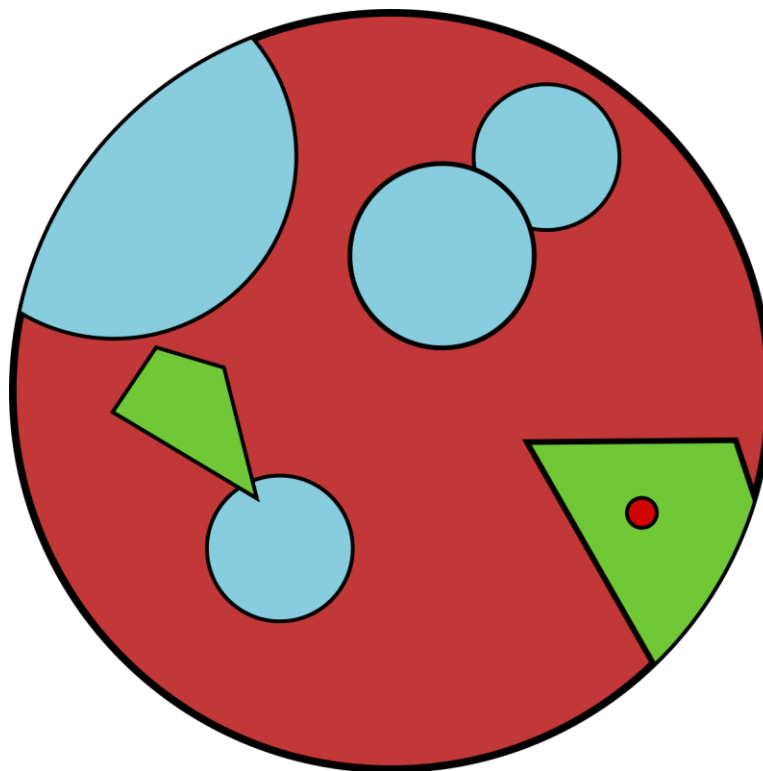
Terrace Rd section, NZ (E Hughes)

Scoria (E Hughes)

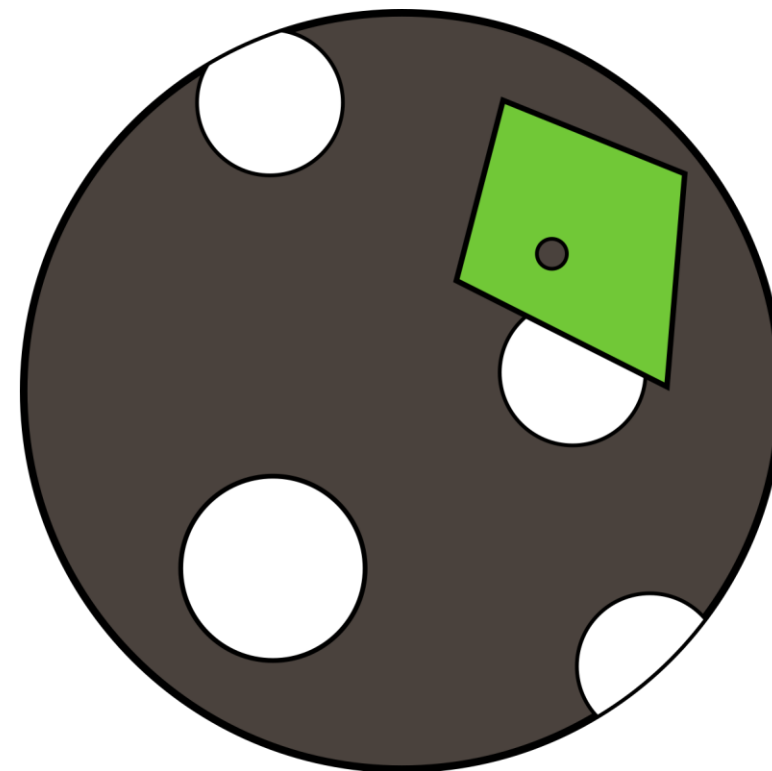


Scoria  
(E Hughes)

Melt (hot)



Glass (cold)



Magma is a multiphase material (melt/glass, crystals, gas)  
chemical + physical properties → eruption style

# Eruption style

## Effusive



Lava flow at Hawaii (USA)

<https://www.flickr.com/photos/jeffgmoore/5464210602>

## Explosive



Explosion at Stromboli (Italy)

[http://www.tboeckel.de/EFSE/efsf\\_stro/Stromboli\\_2009\\_2/stromboli\\_2009\\_2\\_d.htm](http://www.tboeckel.de/EFSE/efsf_stro/Stromboli_2009_2/stromboli_2009_2_d.htm)

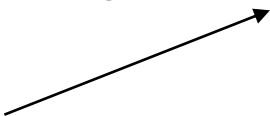


Eruption at Pinatubo (Philippines)

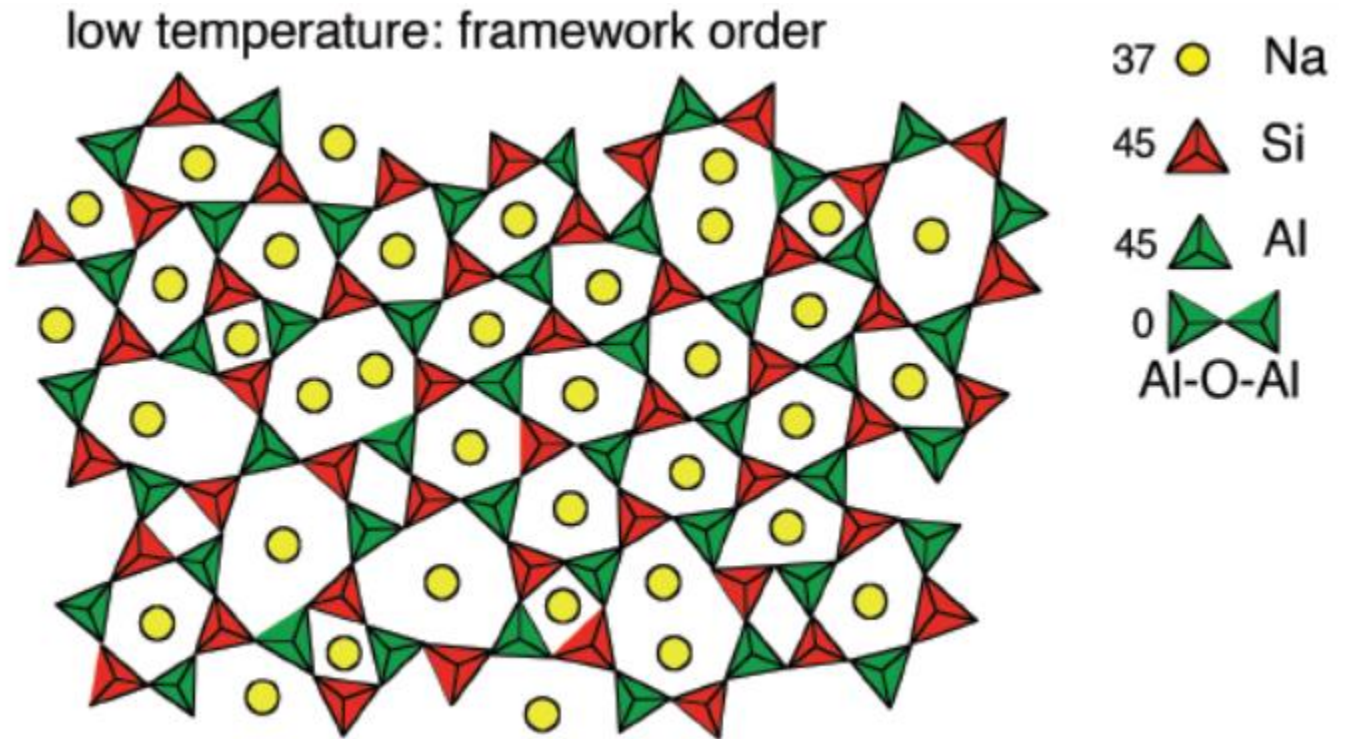
<https://www.britannica.com/science/volcano/Mount-Pinatubo-Philippines-1991>

Low	<b>Gas content:</b> <i>driver for eruption</i>	High
Low	<b>Viscosity:</b> <i>how easily it flows</i>	High

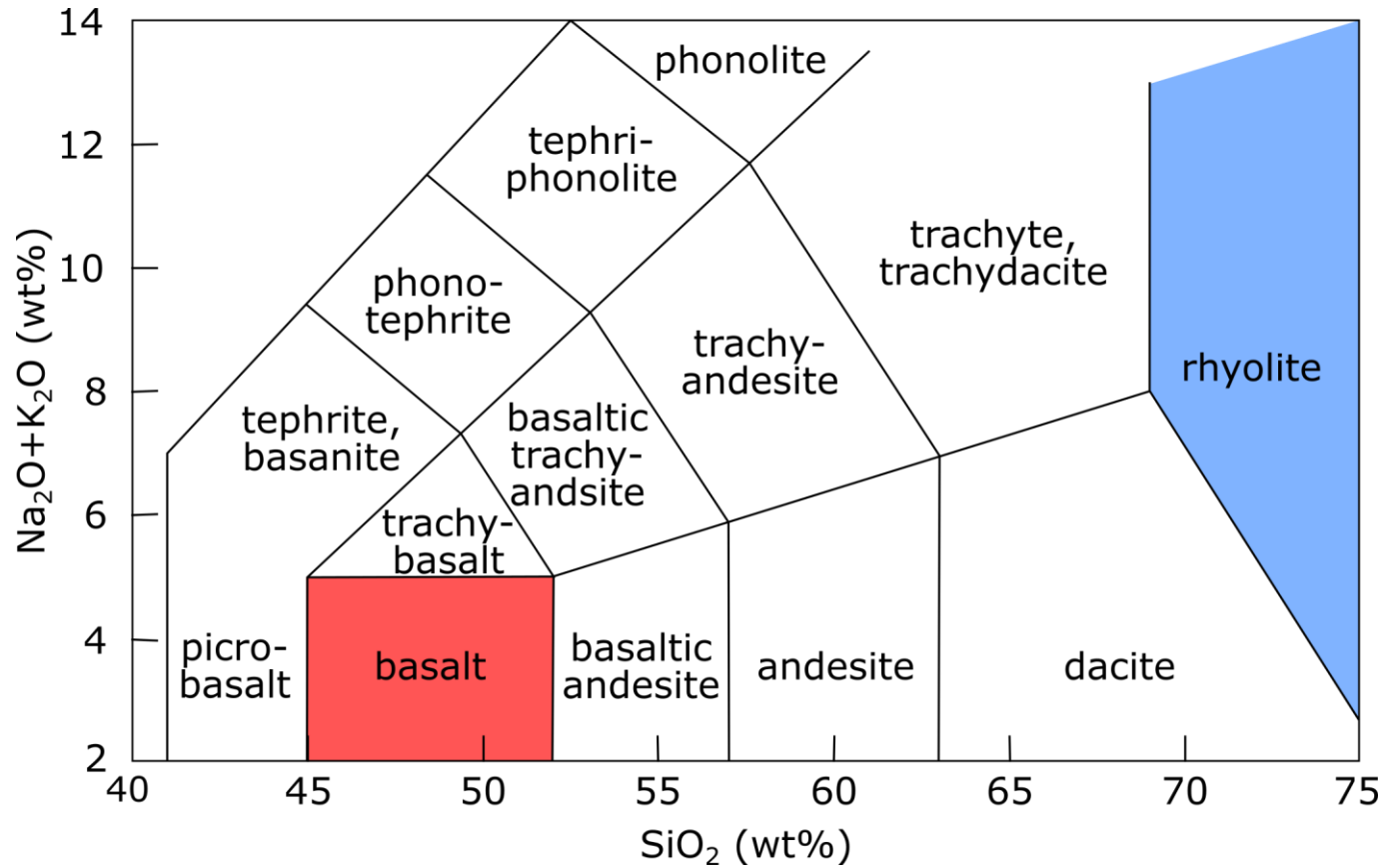
Controlled by:  $\text{SiO}_2$ , T,  
crystal/gas content,  $f\text{O}_2$ ,  
melt composition



- Main component of magma = silicate melt/glass
- Si (and Al) tetrahedra are isolated or form chains
- Plus cations which are network formers or modifiers



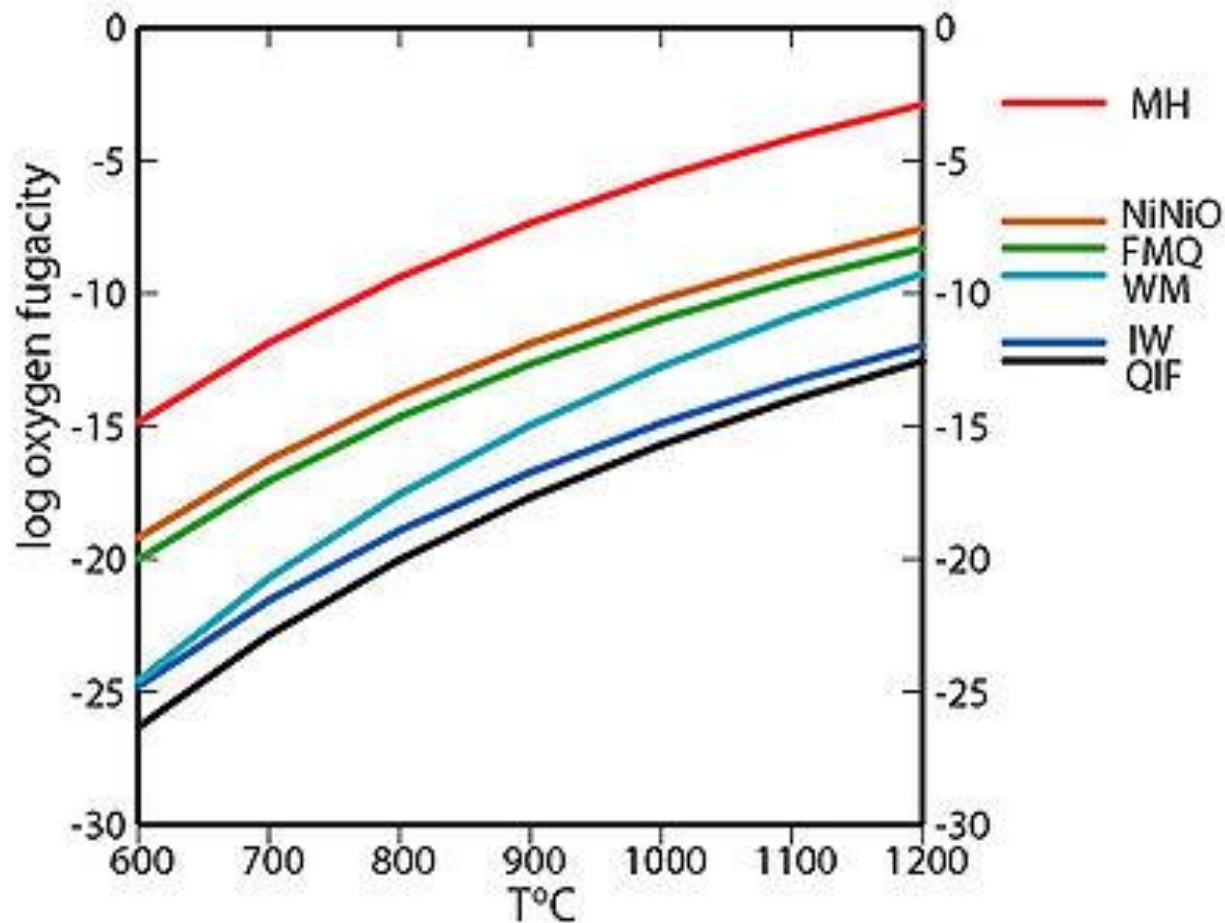
# Magma composition



Majors/minors	$\text{SiO}_2$
	$\text{TiO}_2$
	$\text{Al}_2\text{O}_3$
	$\text{Fe}_2\text{O}_3$
	$\text{FeO}$
	$\text{MgO}$
	$\text{MnO}$
	$\text{CaO}$
	$\text{Na}_2\text{O}$
	$\text{K}_2\text{O}$
	$\text{P}_2\text{O}_5$
Volatiles	$\text{Cl}$
	$\text{S}$
	$\text{F}$
	$\text{H}_2\text{O}$
	$\text{CO}_2$

Elements which go into the vapour phase when pressure decreases

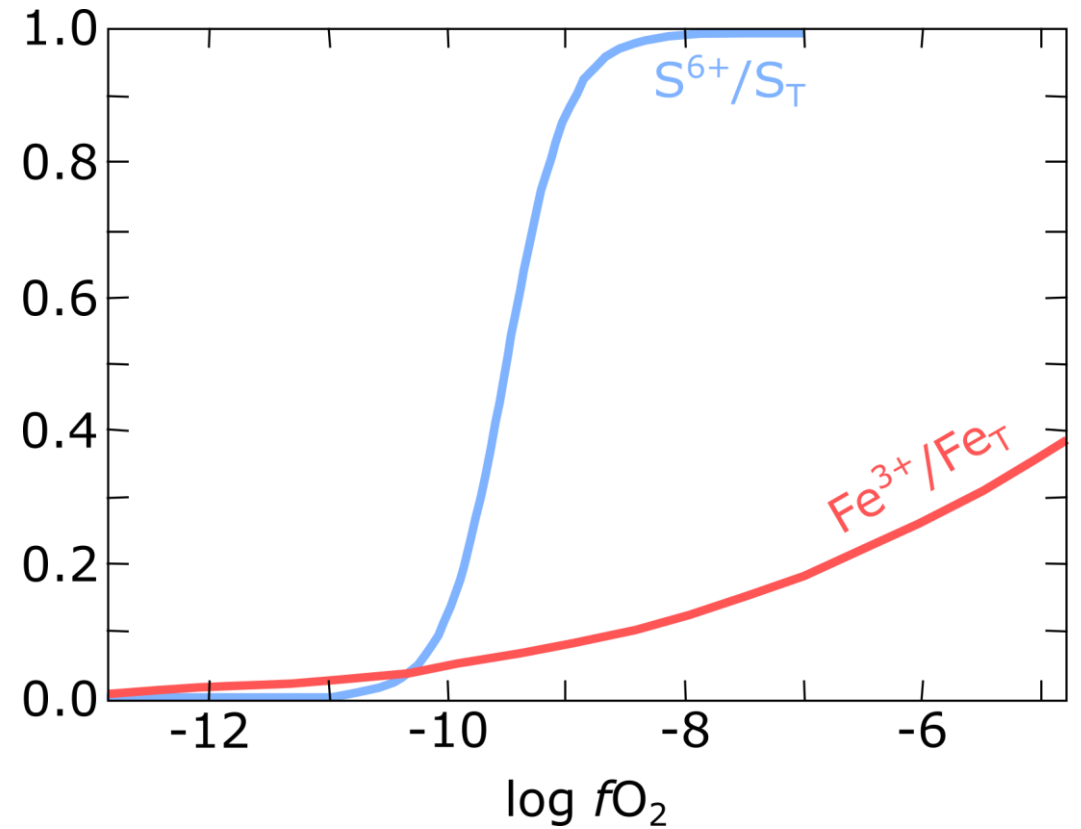
# Oxygen fugacity ( $fO_2$ )



- Equivalent to the partial pressure of O in the system
- $fO_2$  is a control on the physical and chemical properties of the melt
- Effects: phase equilibria, viscosity, gas composition, volatile solubility, etc.
- Controlled by: source and processes

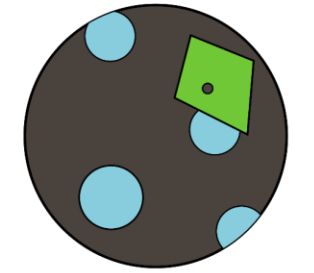
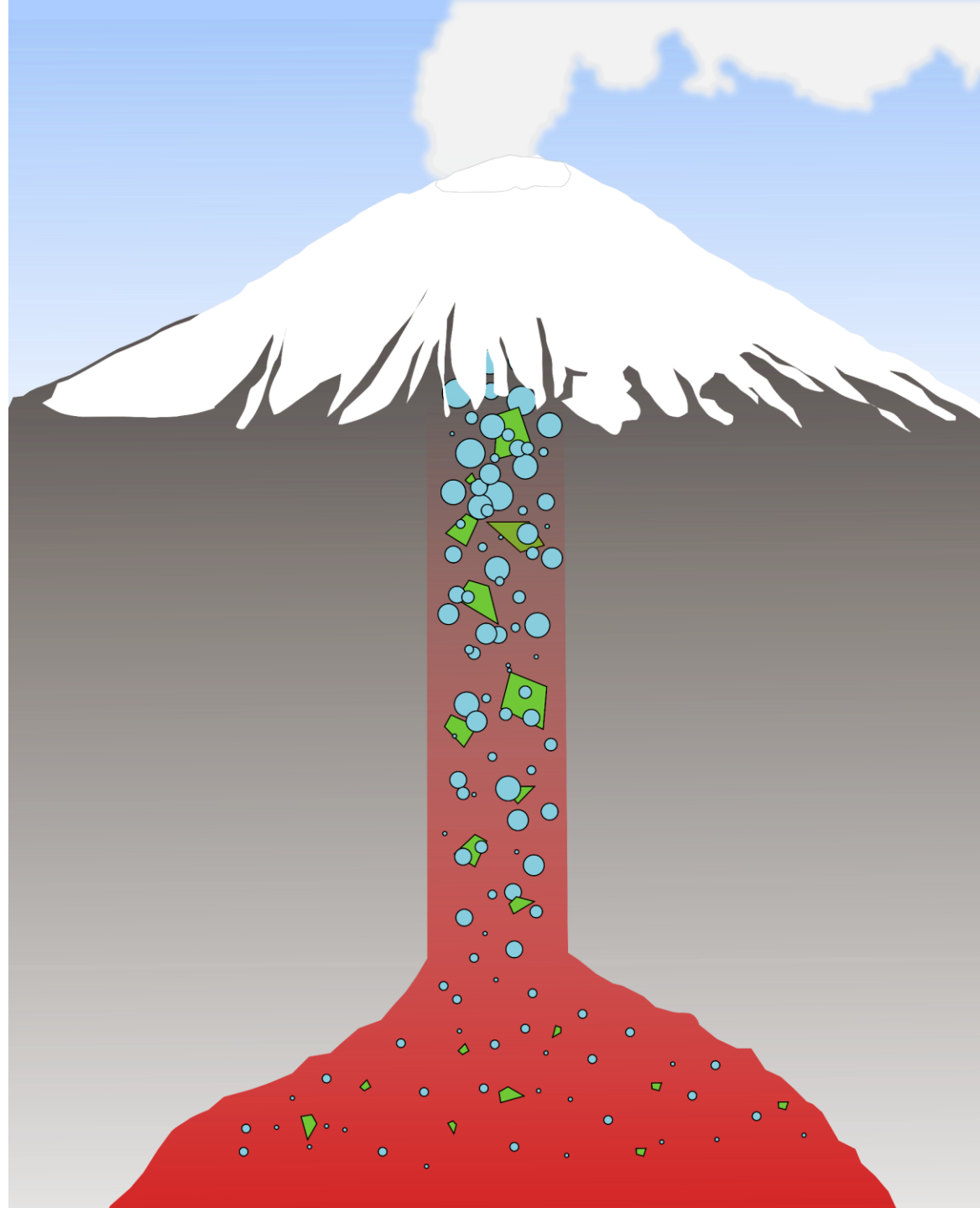
Estimate  $fO_2$  by measuring Fe or S oxidation state in glass

Species	Reduced	Oxidised
S	$S^{2-}$	$S^{6+}$
Fe	$Fe^{2+}$	$Fe^{3+}$

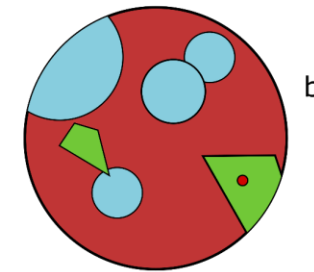


# Sampling magmas using melt inclusions (MIs)

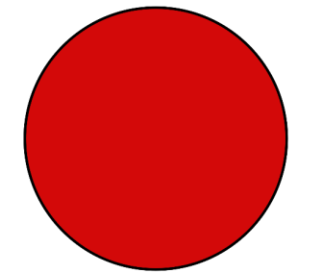
- MIs: tiny pockets of melt, trapped by crystals as they grow from the magma
- Brought to the surface during eruption, MI quenches to a glass



eruption:  
degassed  
melt and  
MIs  
quench

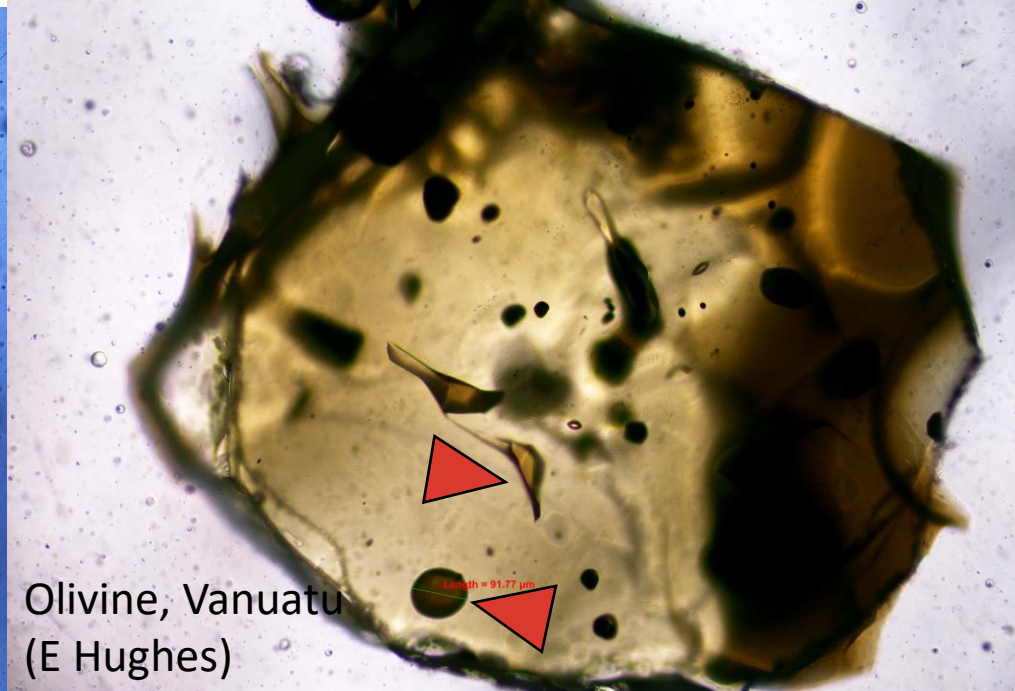
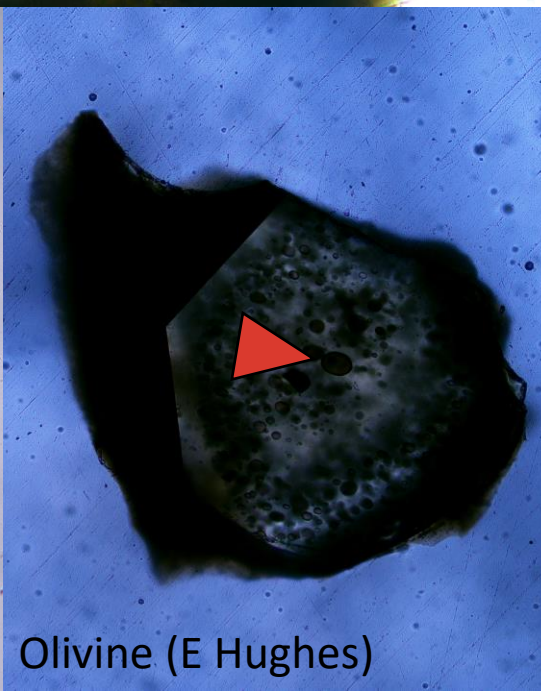
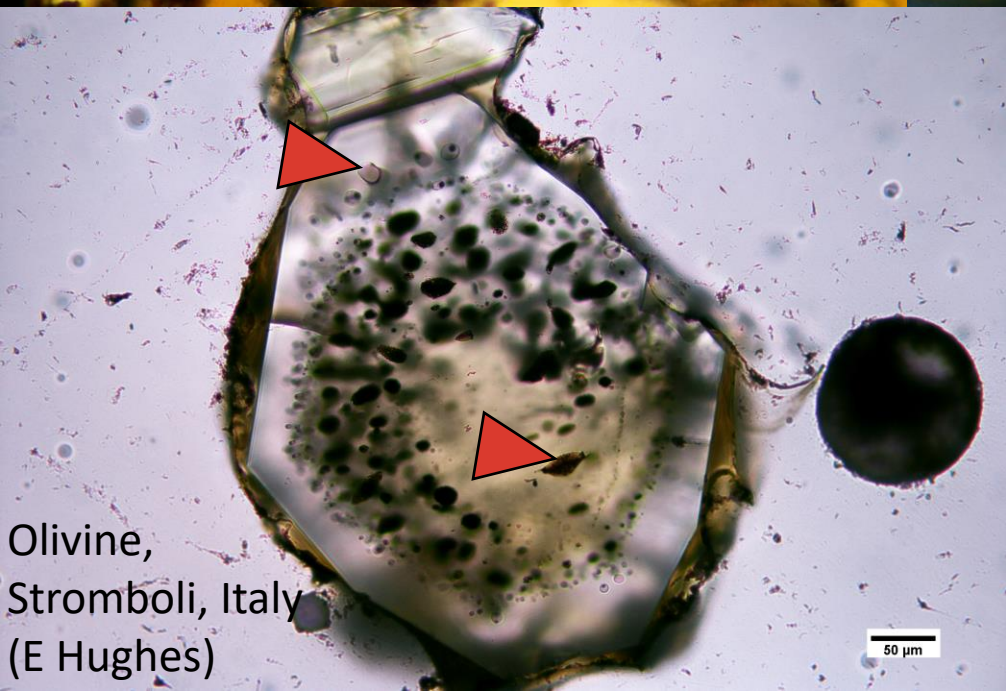
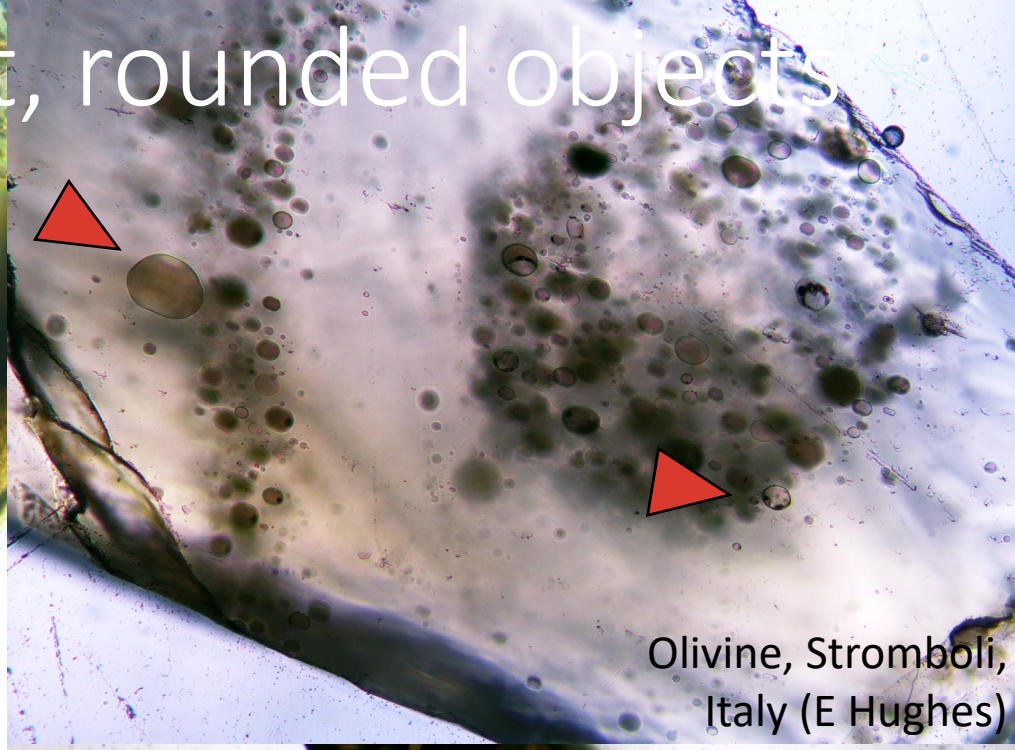
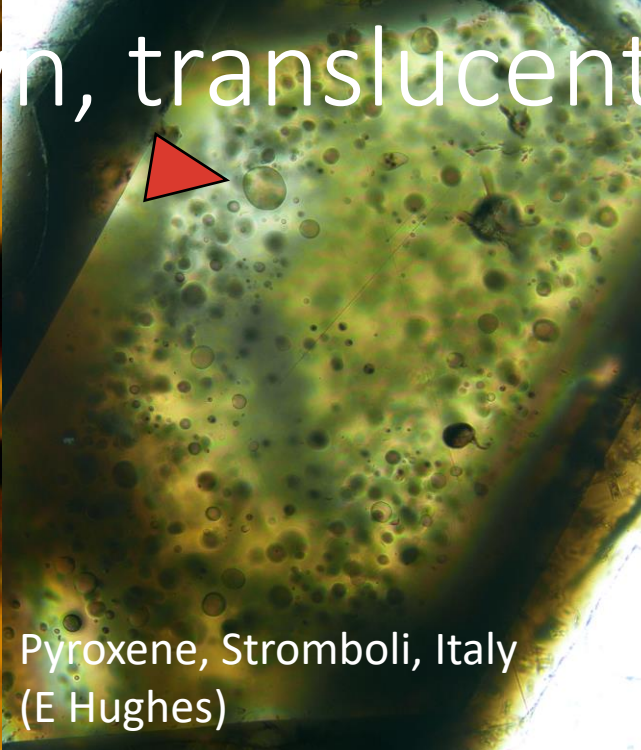


bubbles and  
crystals  
grow; MIs  
form\*

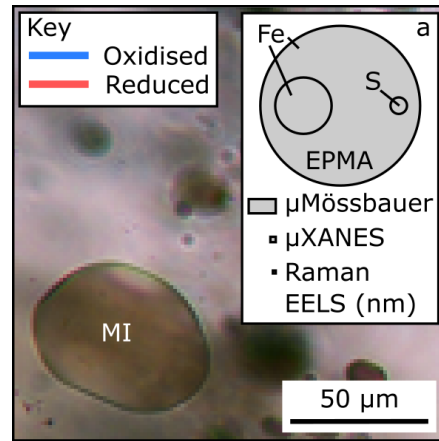


under-  
saturated  
melt

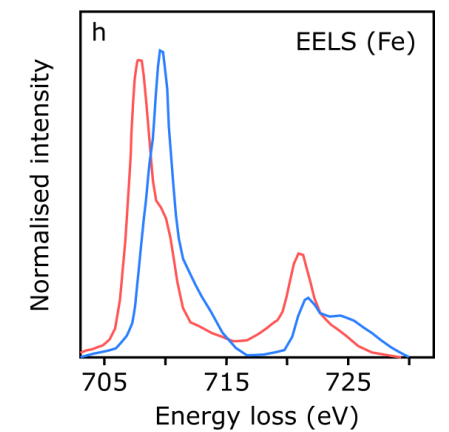
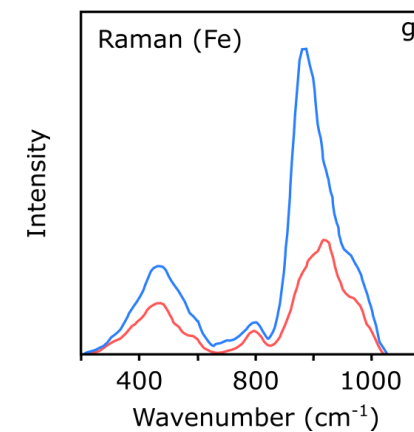
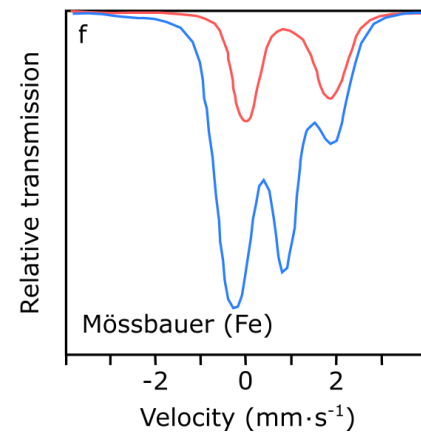
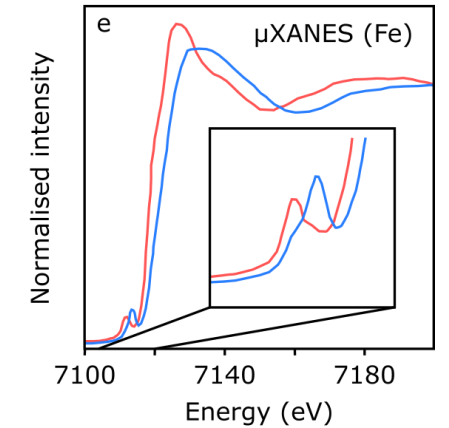
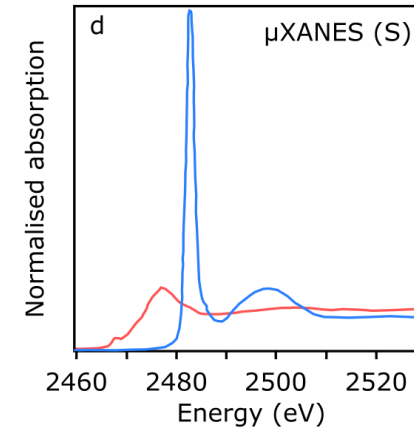
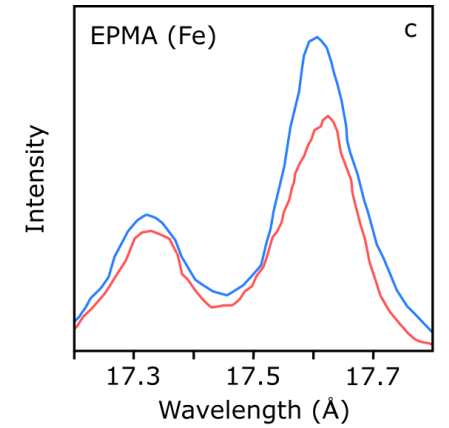
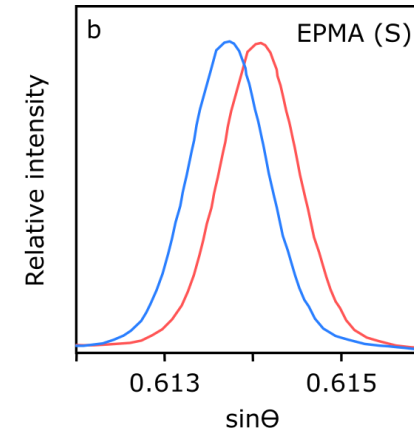
# Example MIs: brown, translucent, rounded objects

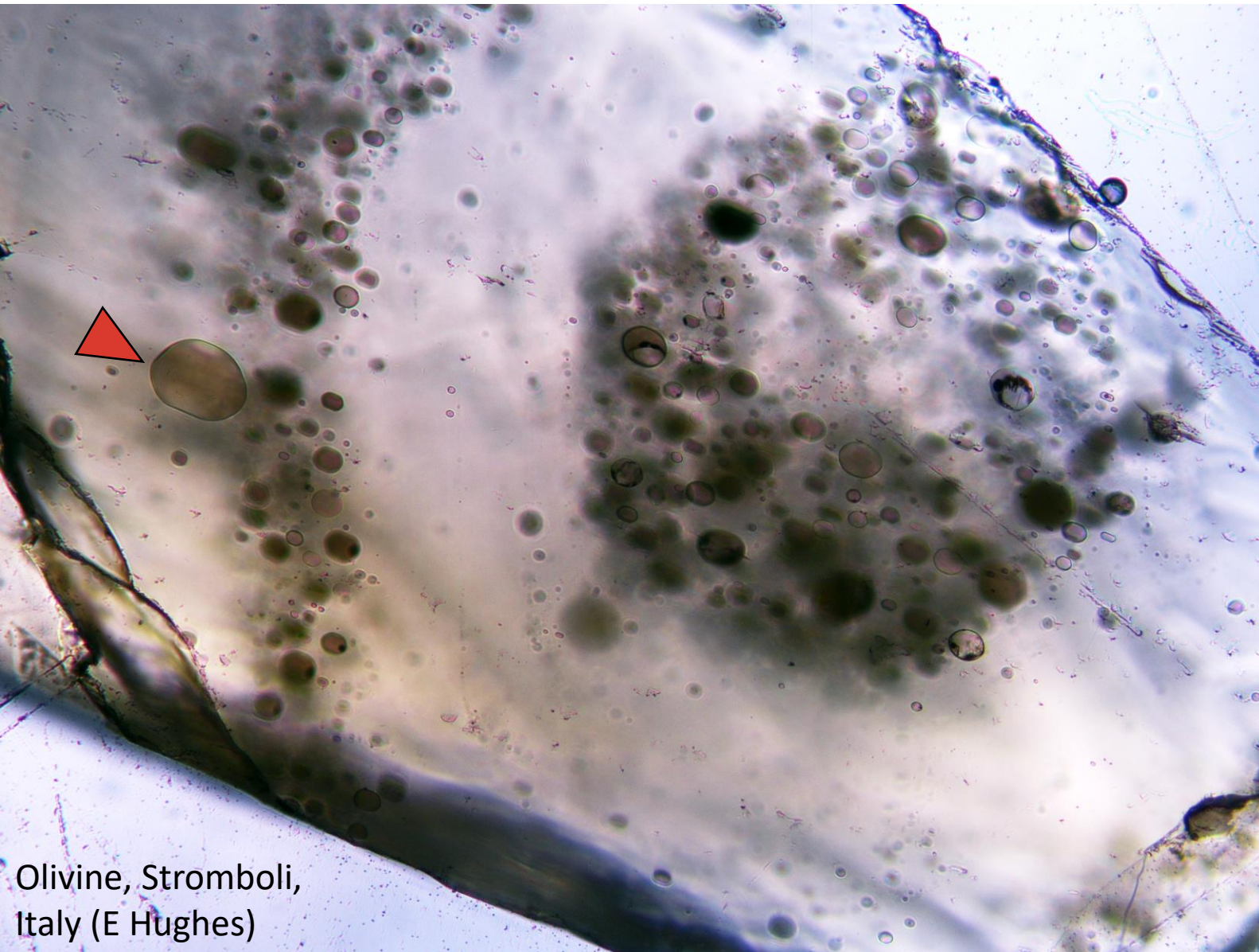


# Different microanalytical techniques for measuring Fe or S oxidation state in silicate glass at high spatial resolution (1–100 $\mu\text{m}$ )



- b) Wilke *et al.* (2011)
- c) Jugo *et al.* (2010)
- d) Hughes *et al.* (2018)
- e) Cottrell *et al.* (2009)
- f) Cottrell *et al.* (2009)
- g) Di Genova *et al.* (2016)
- h) Burgess *et al.* (2016)





Olivine, Stromboli,  
Italy (E Hughes)

- Glass is unstable and can be damaged during analysis
- Can generate incorrect data and interpretations

- Experimental observations
- Mechanisms

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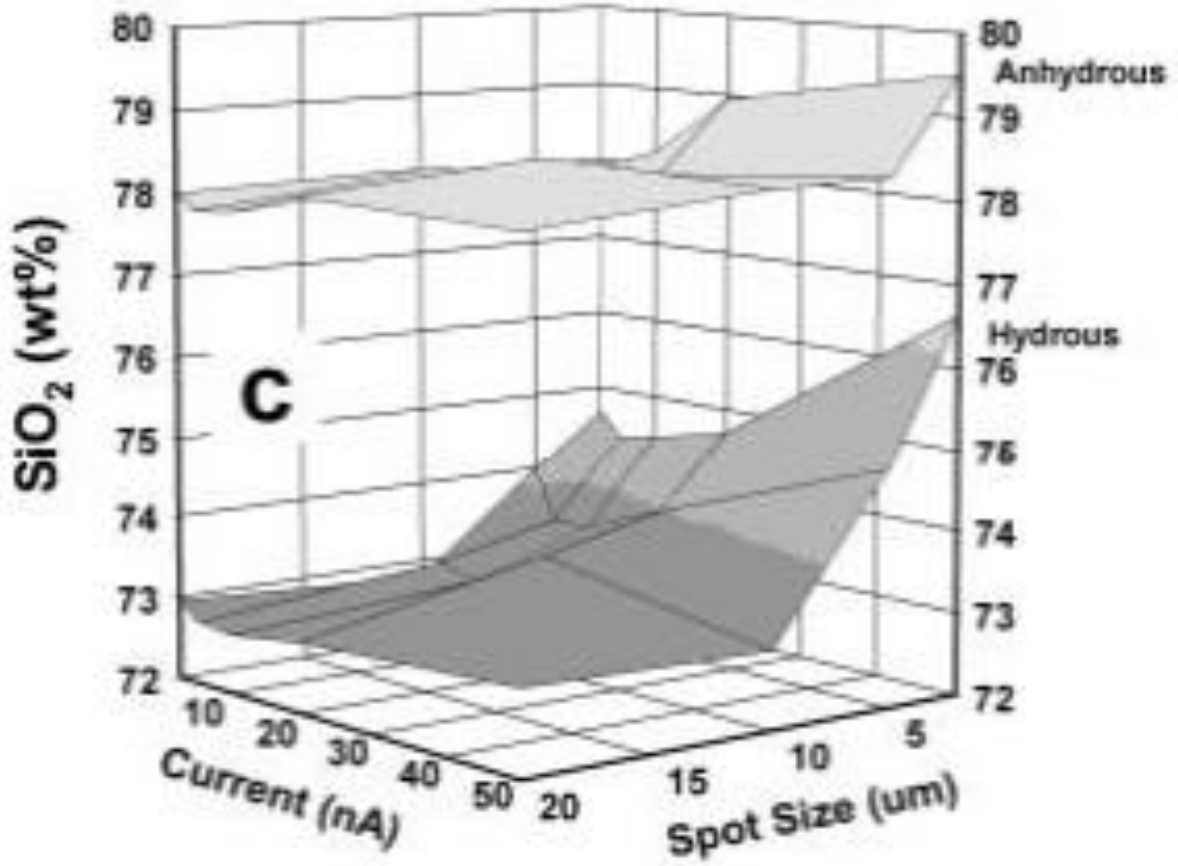
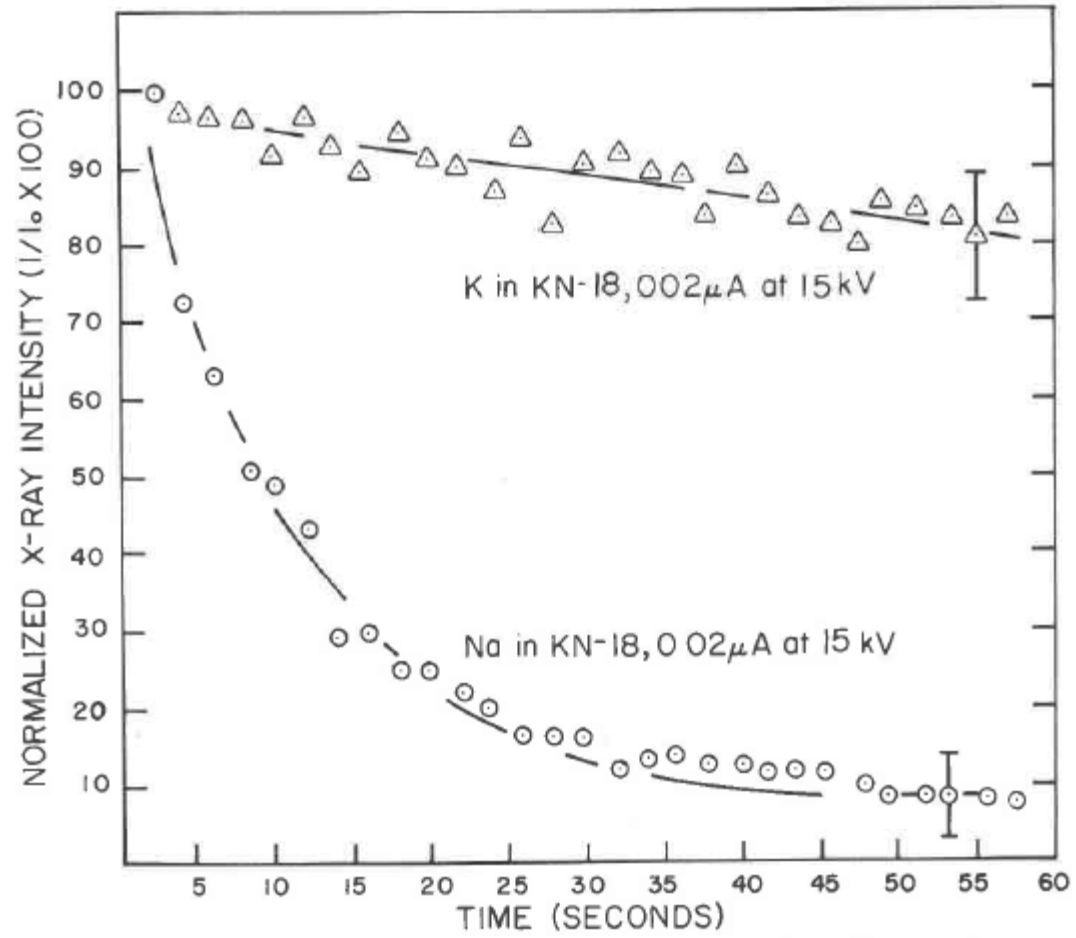
Technique	Fe	S
EPMA	Y	Y
XANES	Y	Y
EELS	Y	
Raman	Y	N
Mössbauer	N	

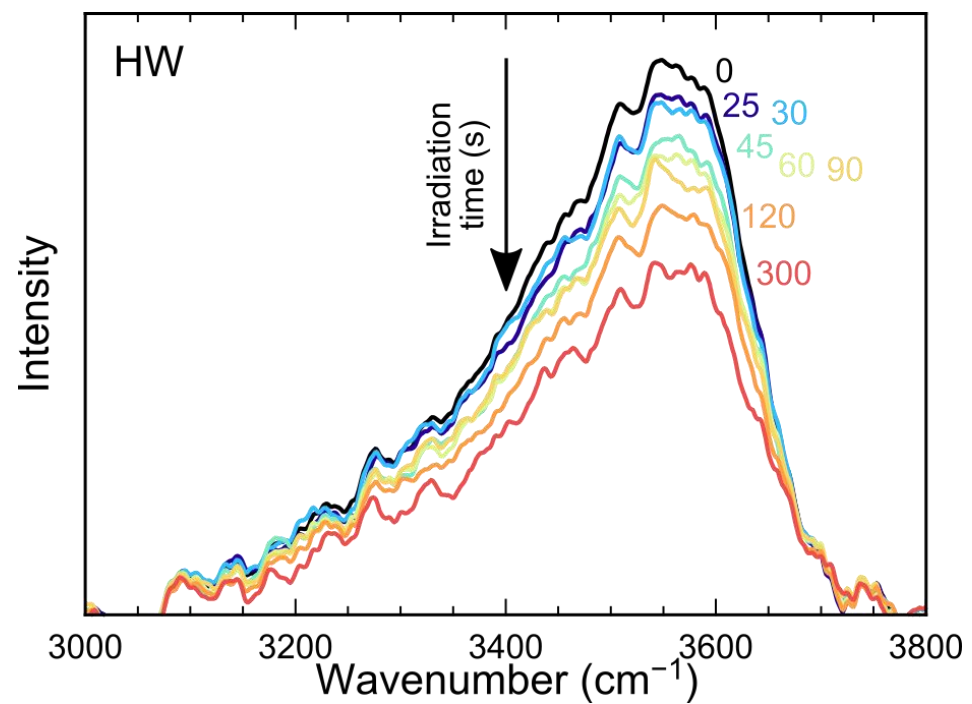
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# 1. Mobile elements migrate

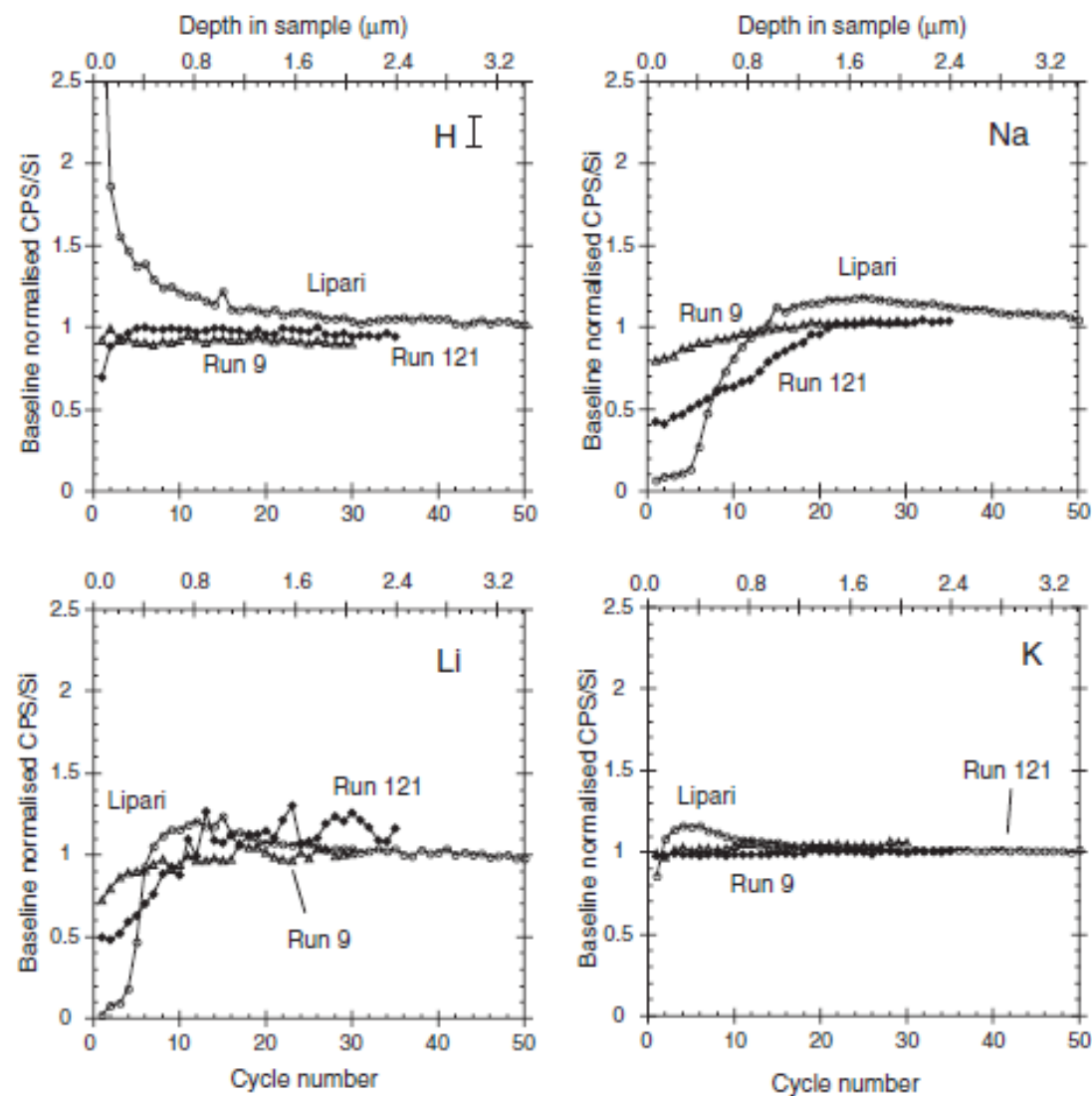
# EPMA damage

Mobile elements decrease in concentration during analysis, immobile elements increase

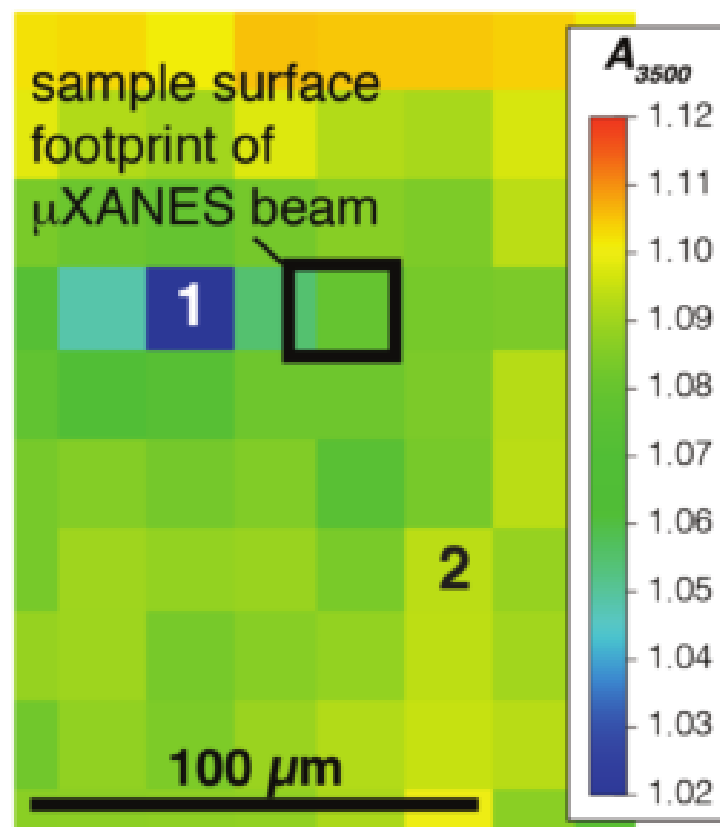


EPMA damage    Decrease in H<sub>2</sub>O concentration

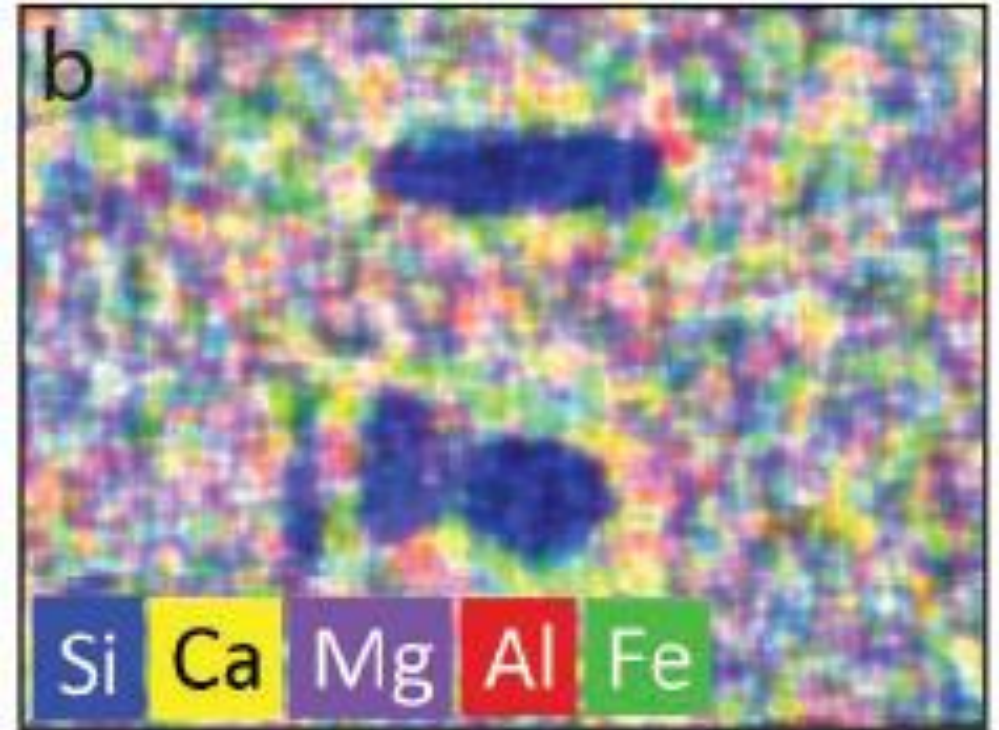
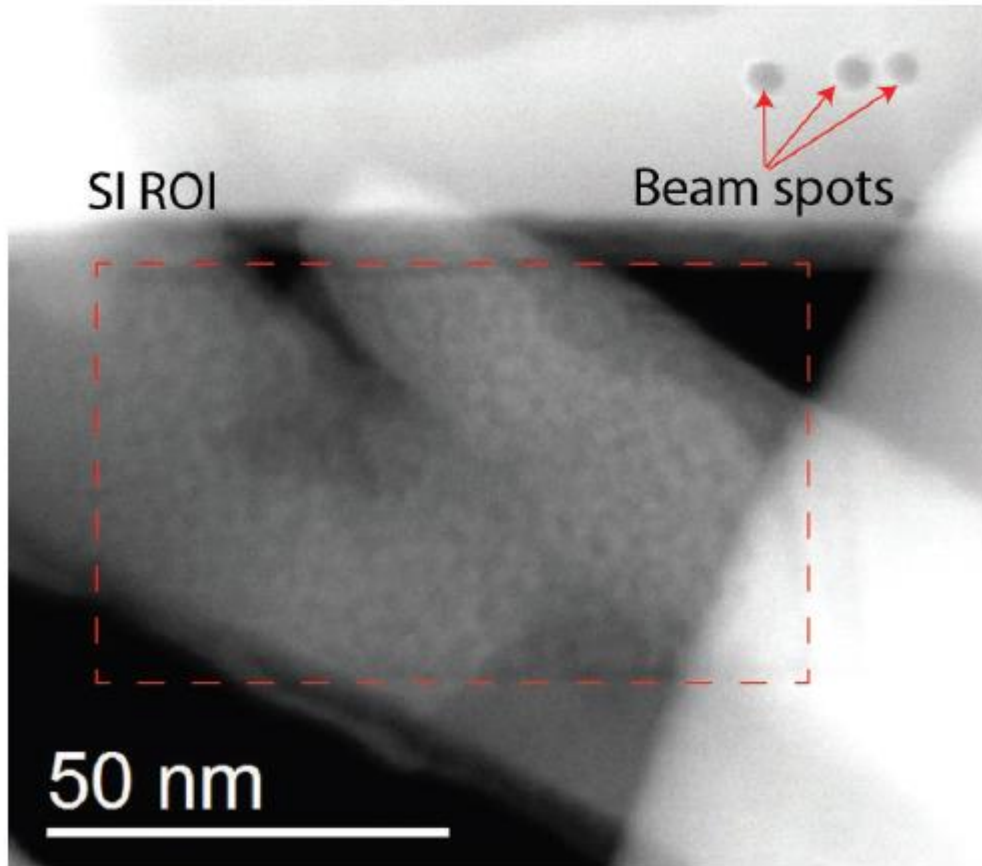
## EPMA damage Mobile elements migrate down into the sample



XANES damage     $\text{H}_2\text{O}$  migrates away



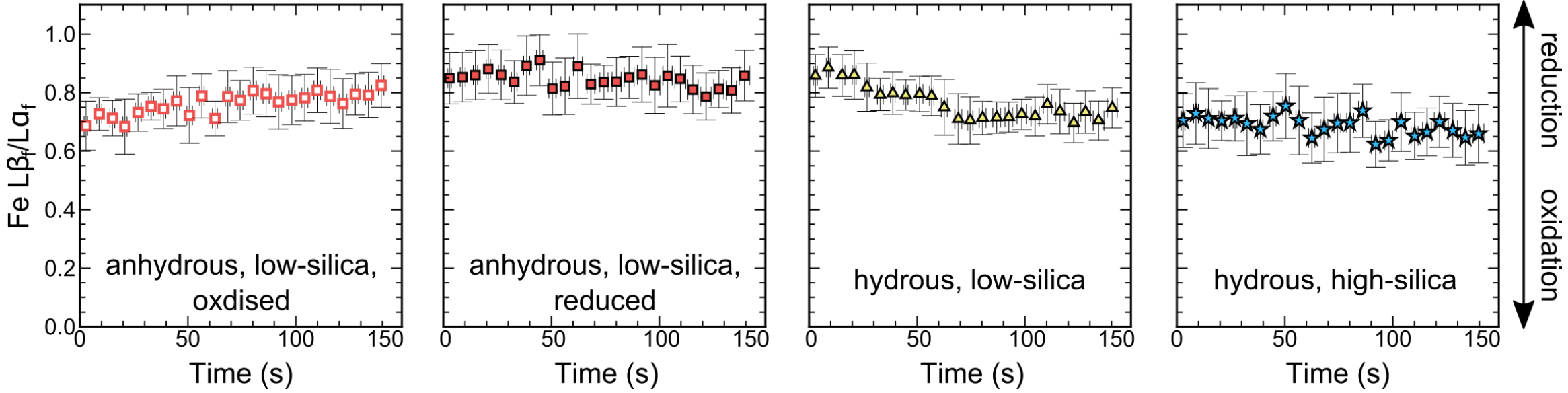
EELS damage Density and composition changes,  
most elements migrate away



1. Mobile elements migrate
2. Fe oxidises and reduces depending on glass composition and analytical conditions

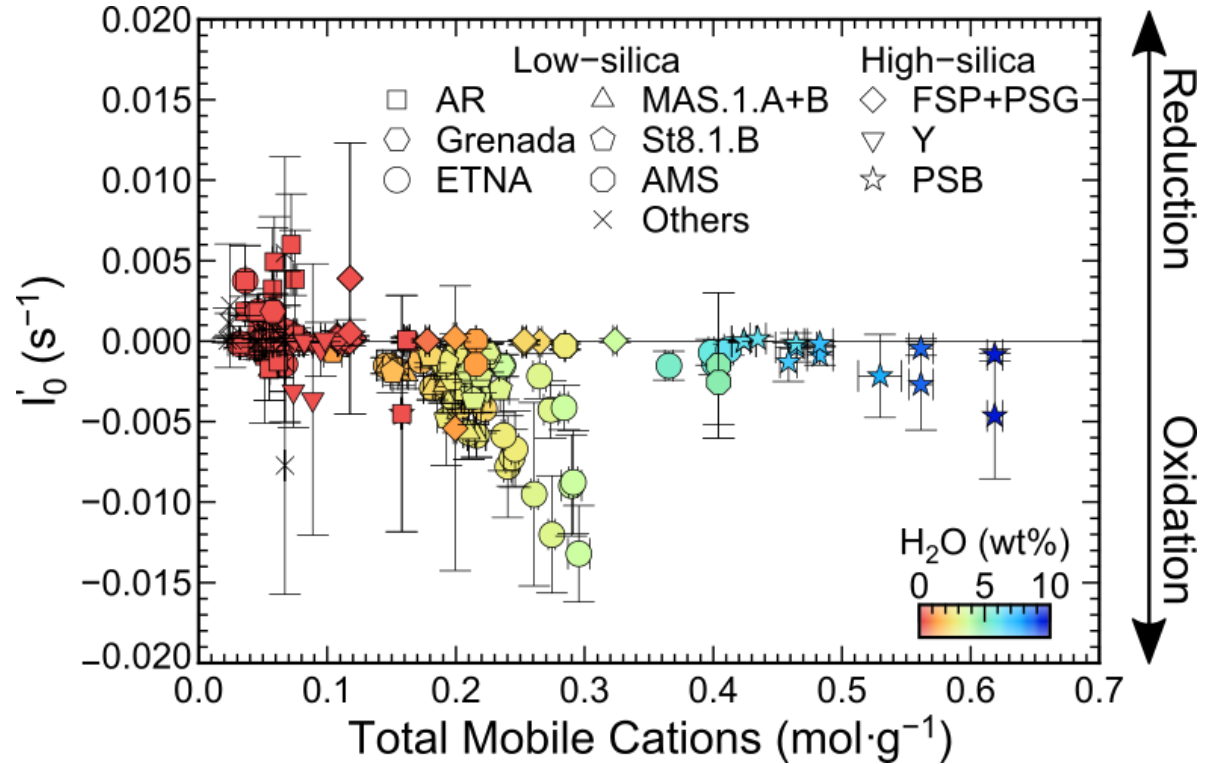
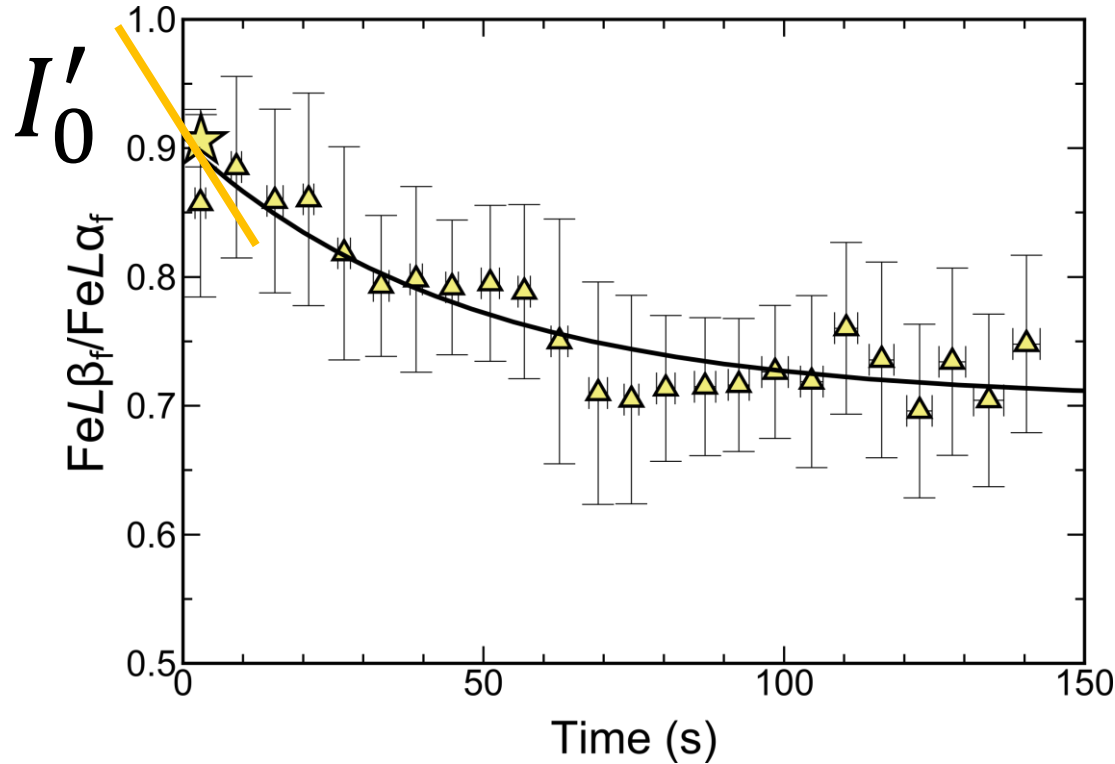
# EPMA damage Reduction and oxidation of Fe

## *Composition*



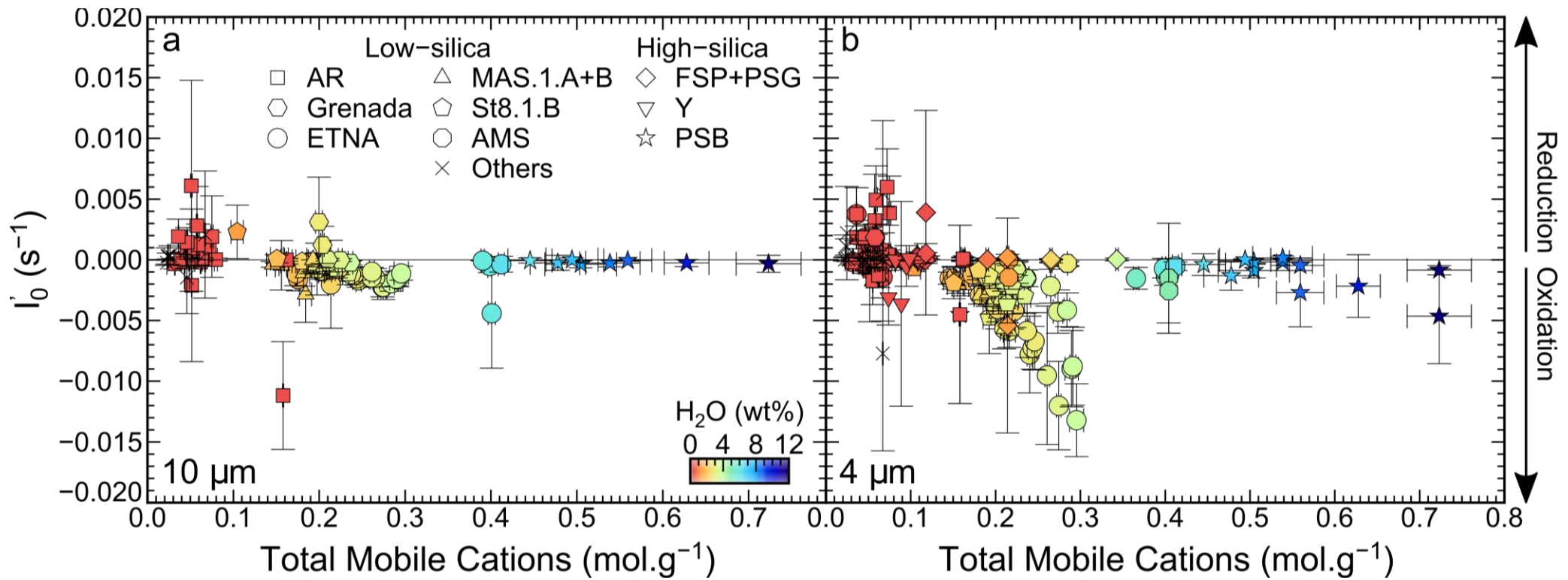
# EPMA damage Change in oxidation state is exponential

## Composition



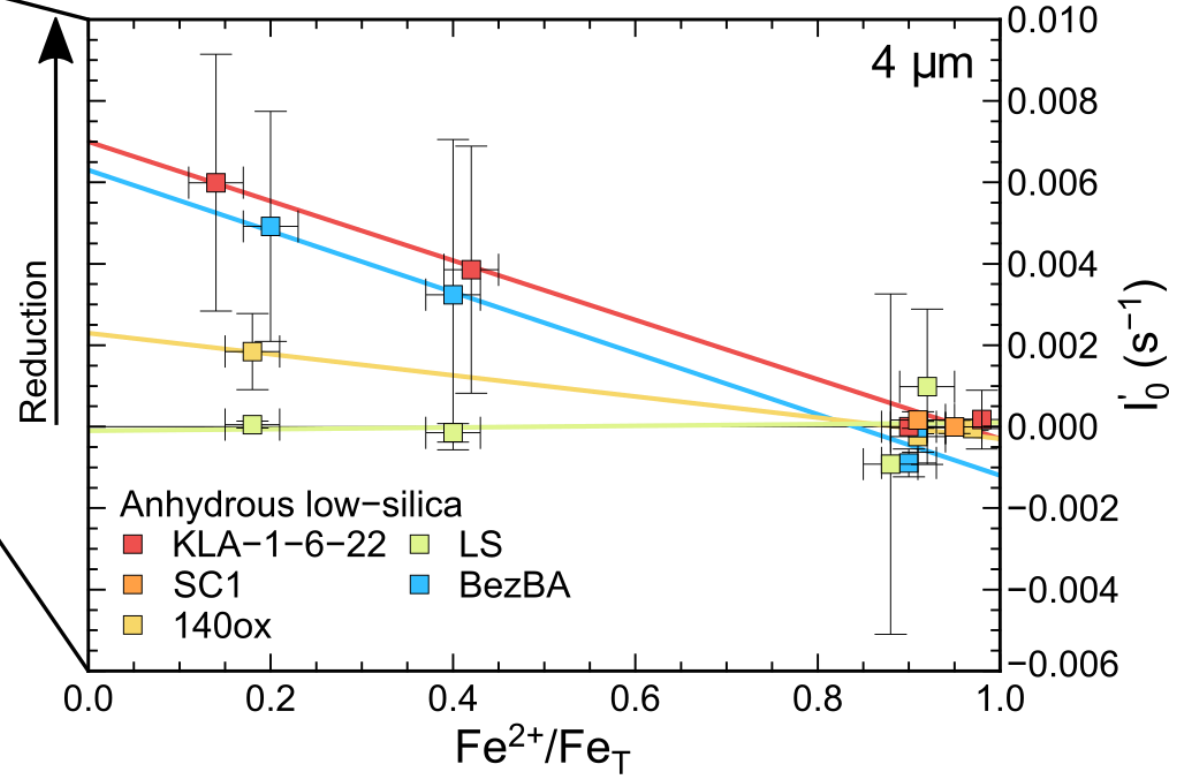
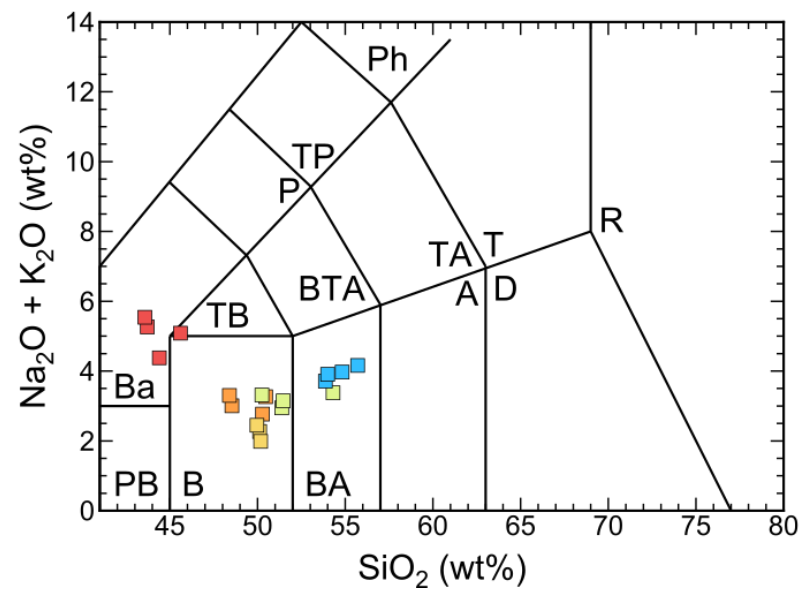
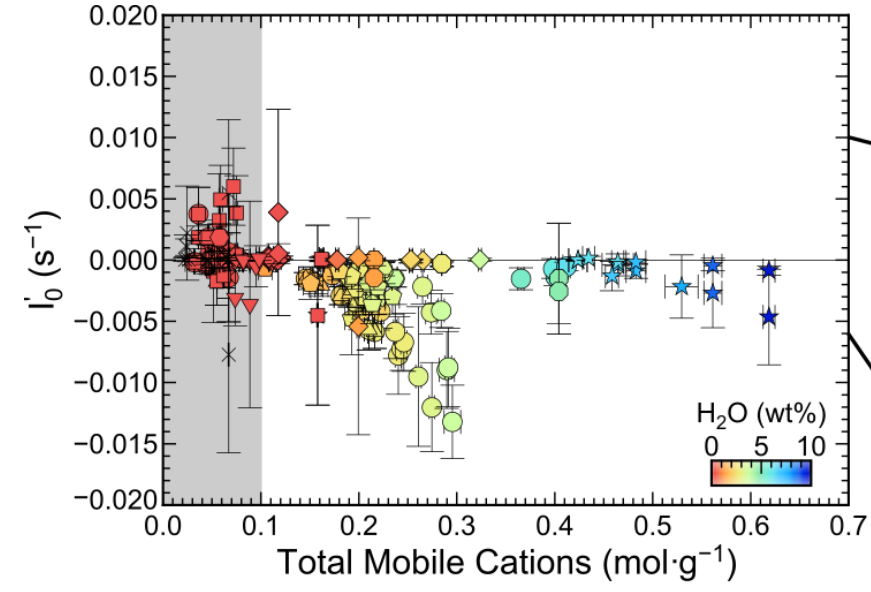
$$\text{TMC} = \text{molar sum } \text{H}_2\text{O} + \text{Na}_2\text{O} + \text{K}_2\text{O}$$

EPMA damage *Beam size* Increase beam density (decrease beam size, increase beam current, and decrease accelerating voltage) increases rate of change



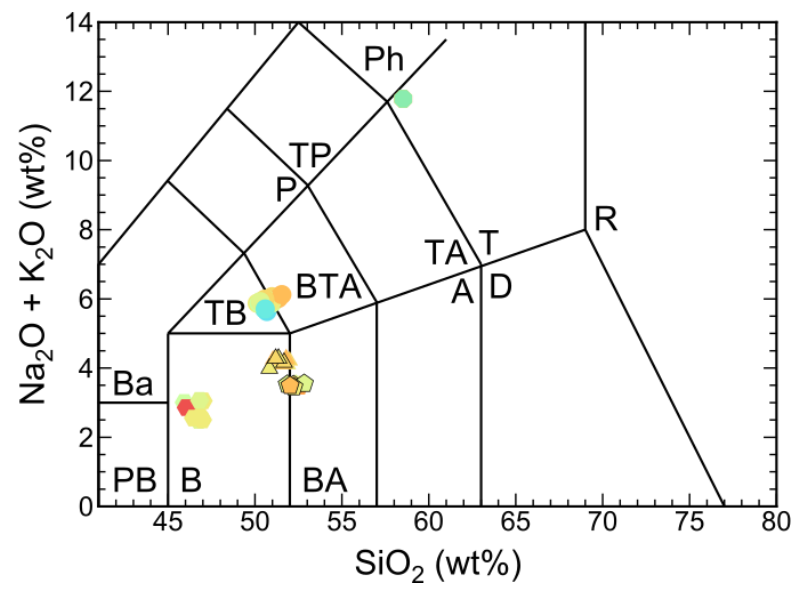
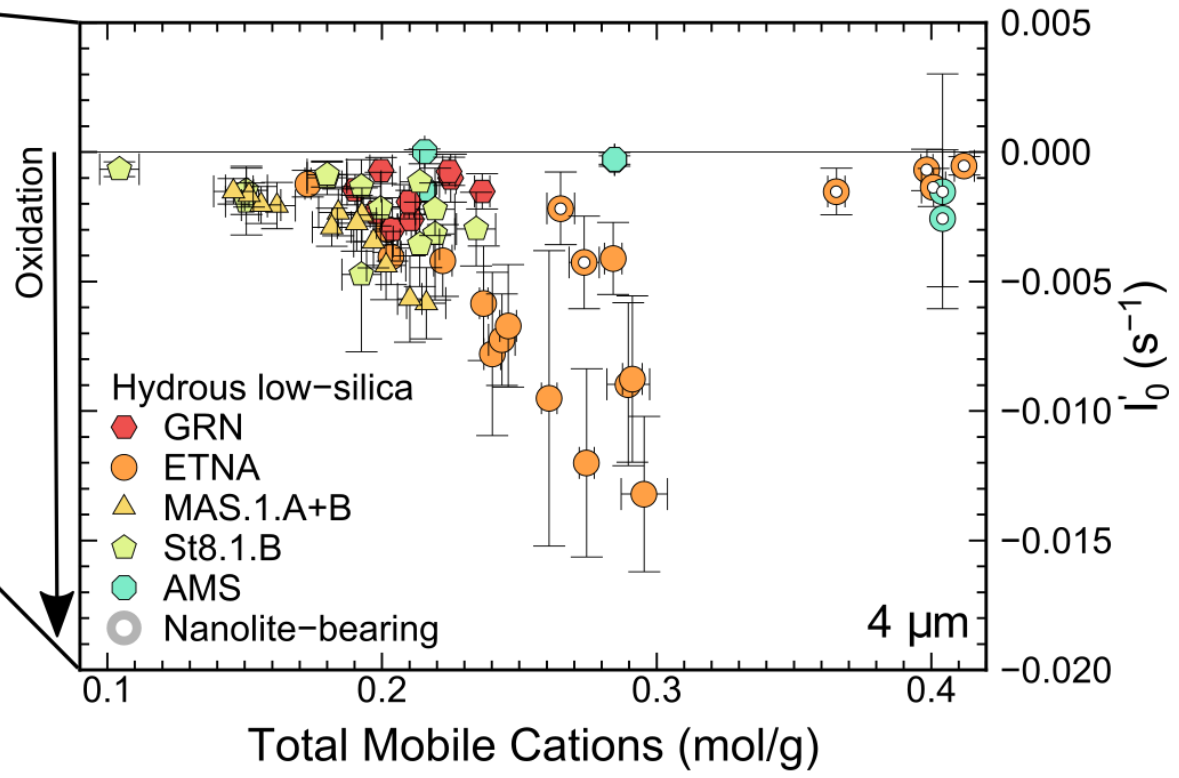
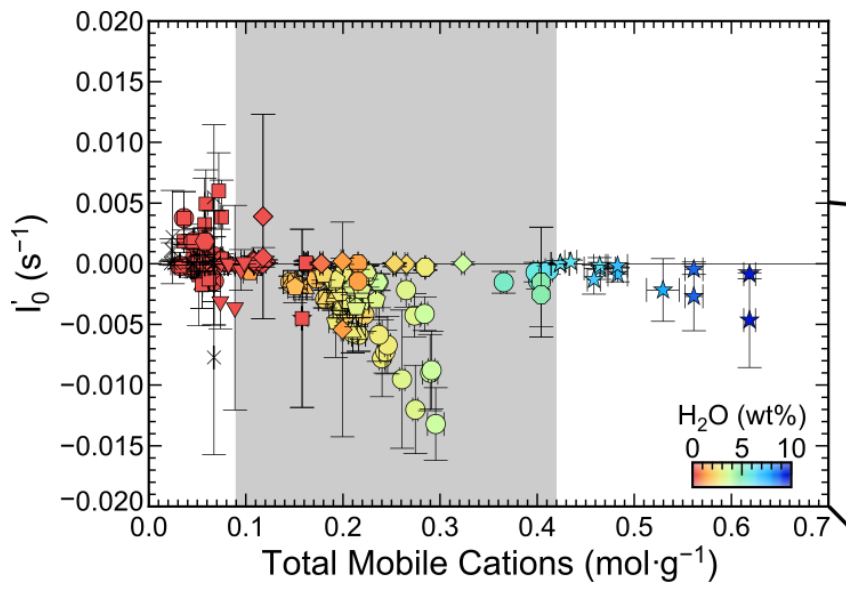
# EPMA damage *Composition*

Anhydrous basalts reduce  
Rate of reduction depends on initial  
 $Fe^{2+}/Fe_T$



# EPMA damage *Composition*

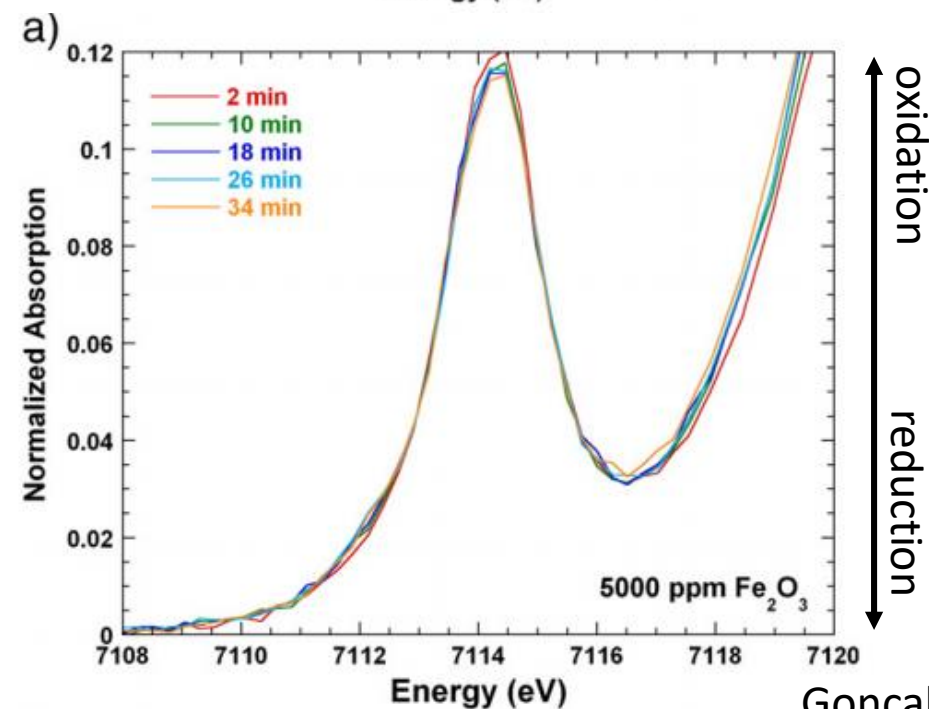
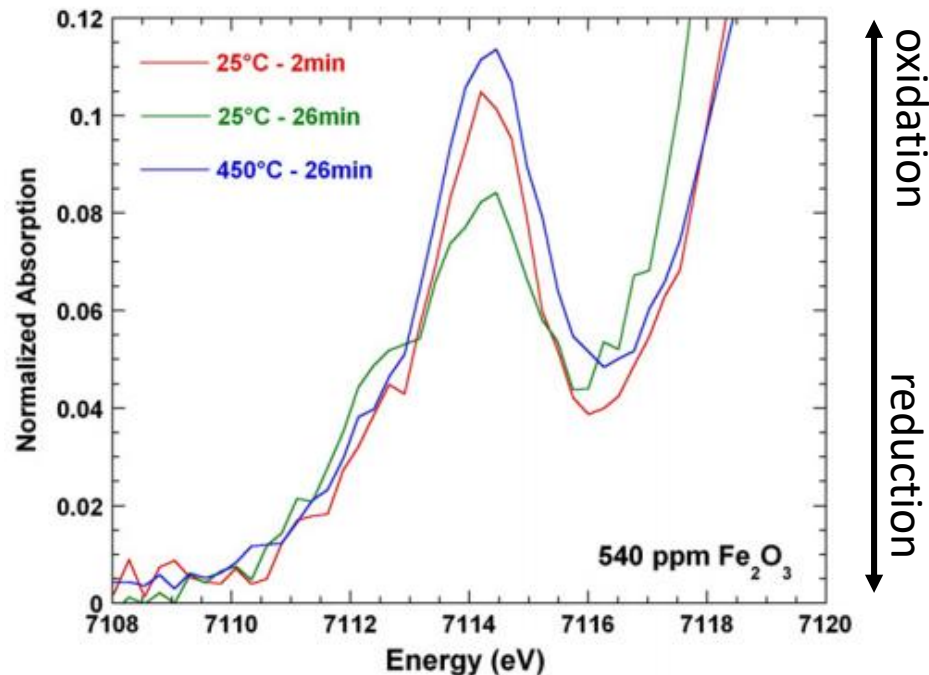
Hydrous basalts oxidise  
Rate of oxidation depends on H<sub>2</sub>O  
concentration



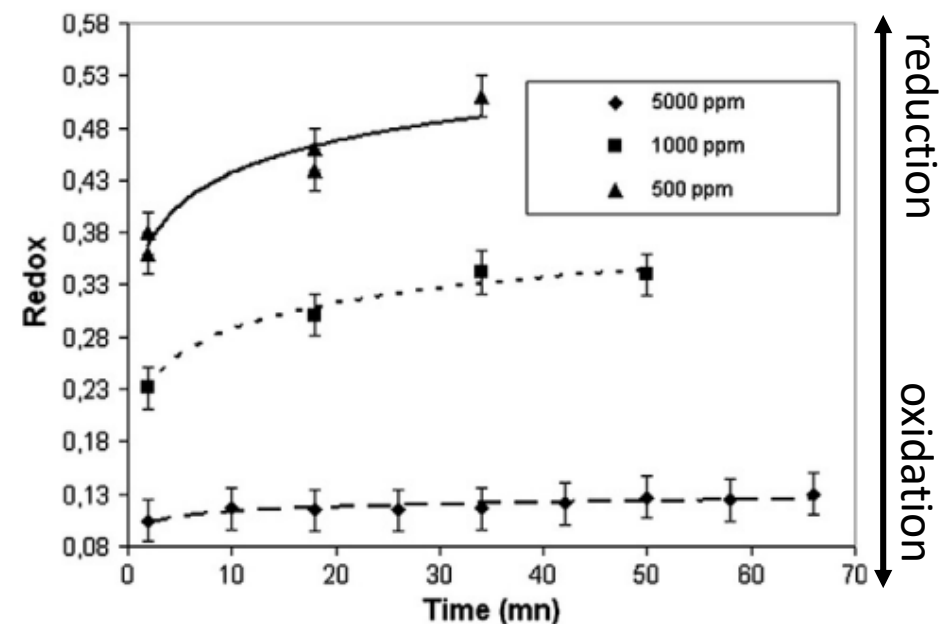
# XANES damage *Fe content*

Low Fe glasses  
reduce

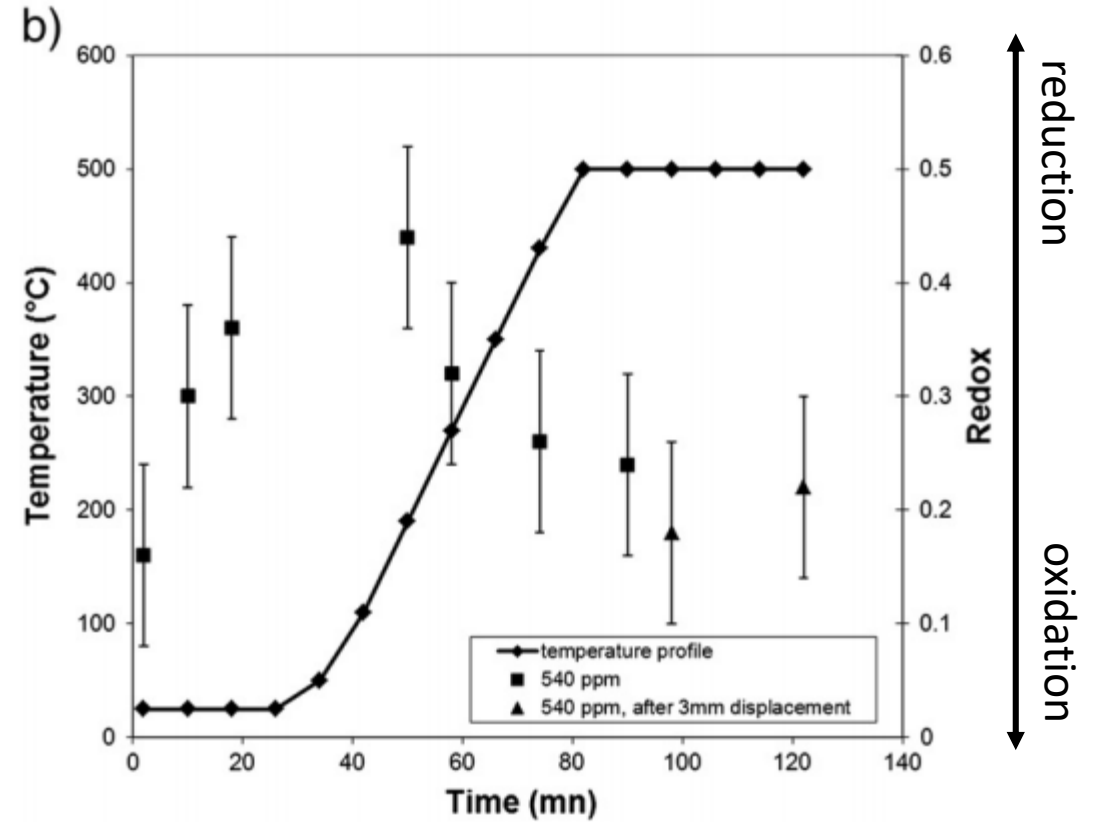
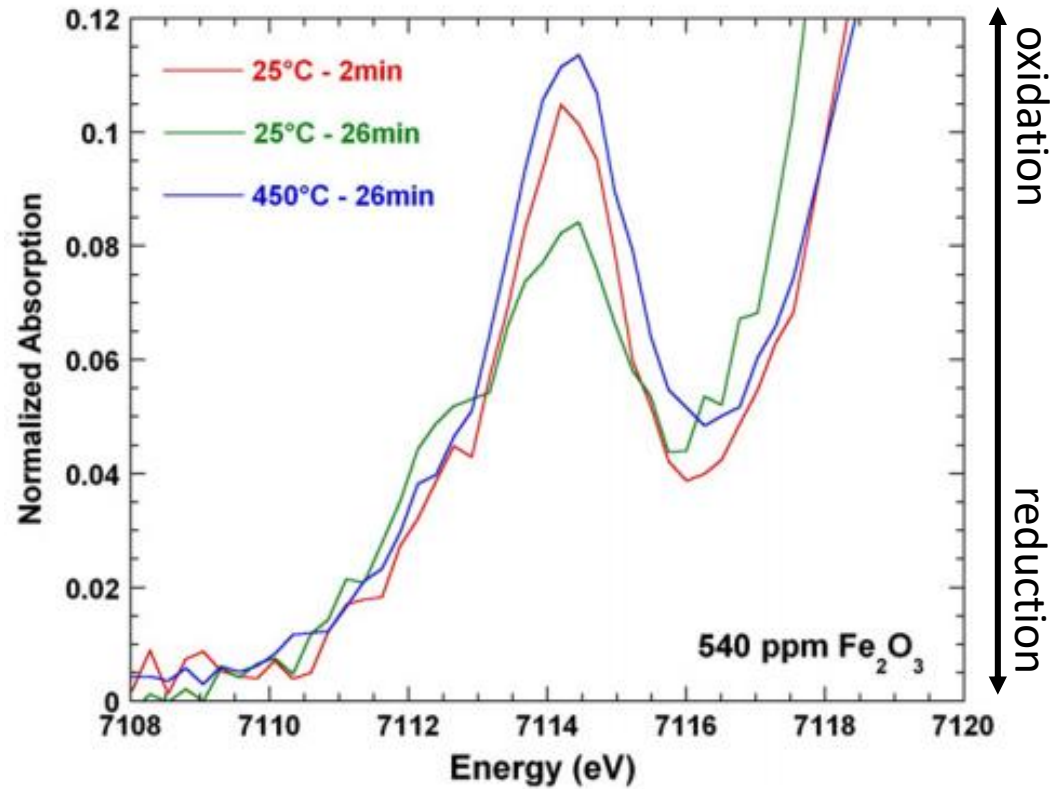
Same absolute  
amount of Fe  
reduces but  
smaller effect  
on oxidation  
state at higher  
Fe



## XANES data

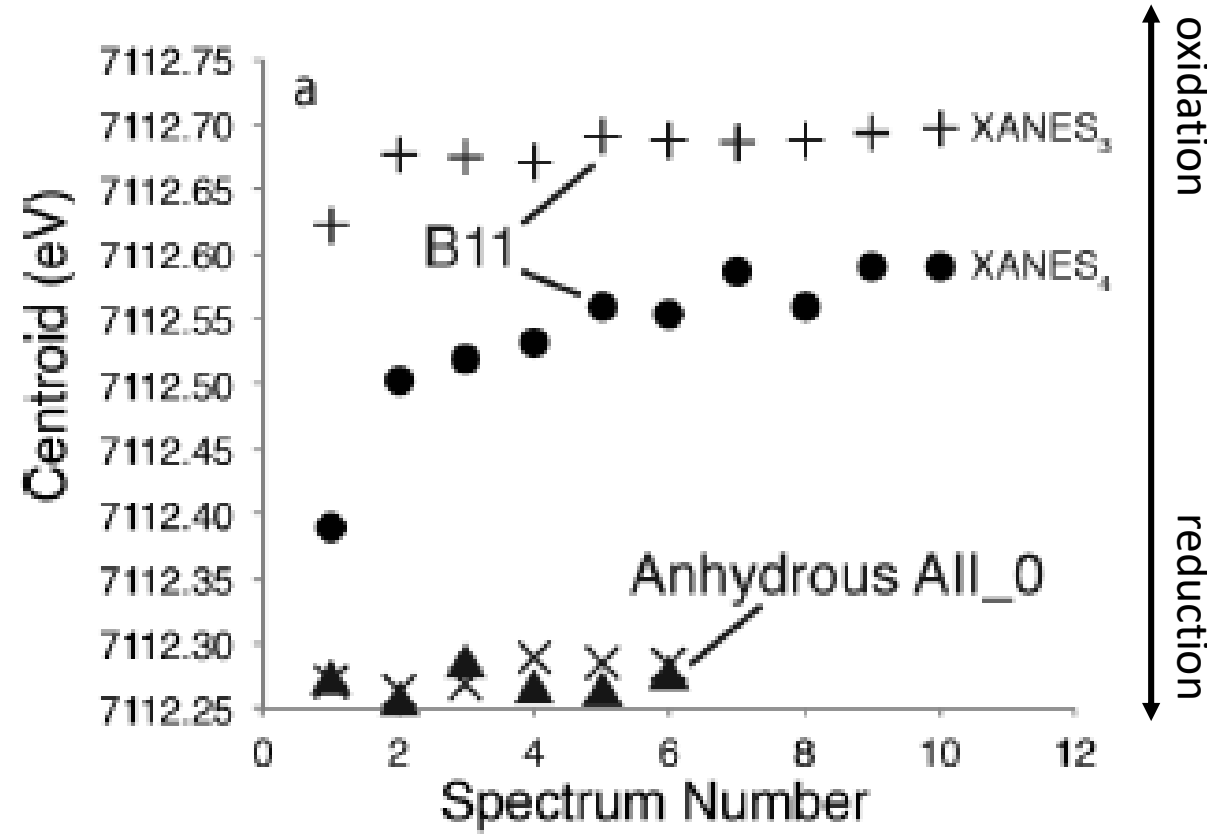


XANES damage Temperature Reduction does not occur/is reversed at high temperature



XANES damage  
*Composition*

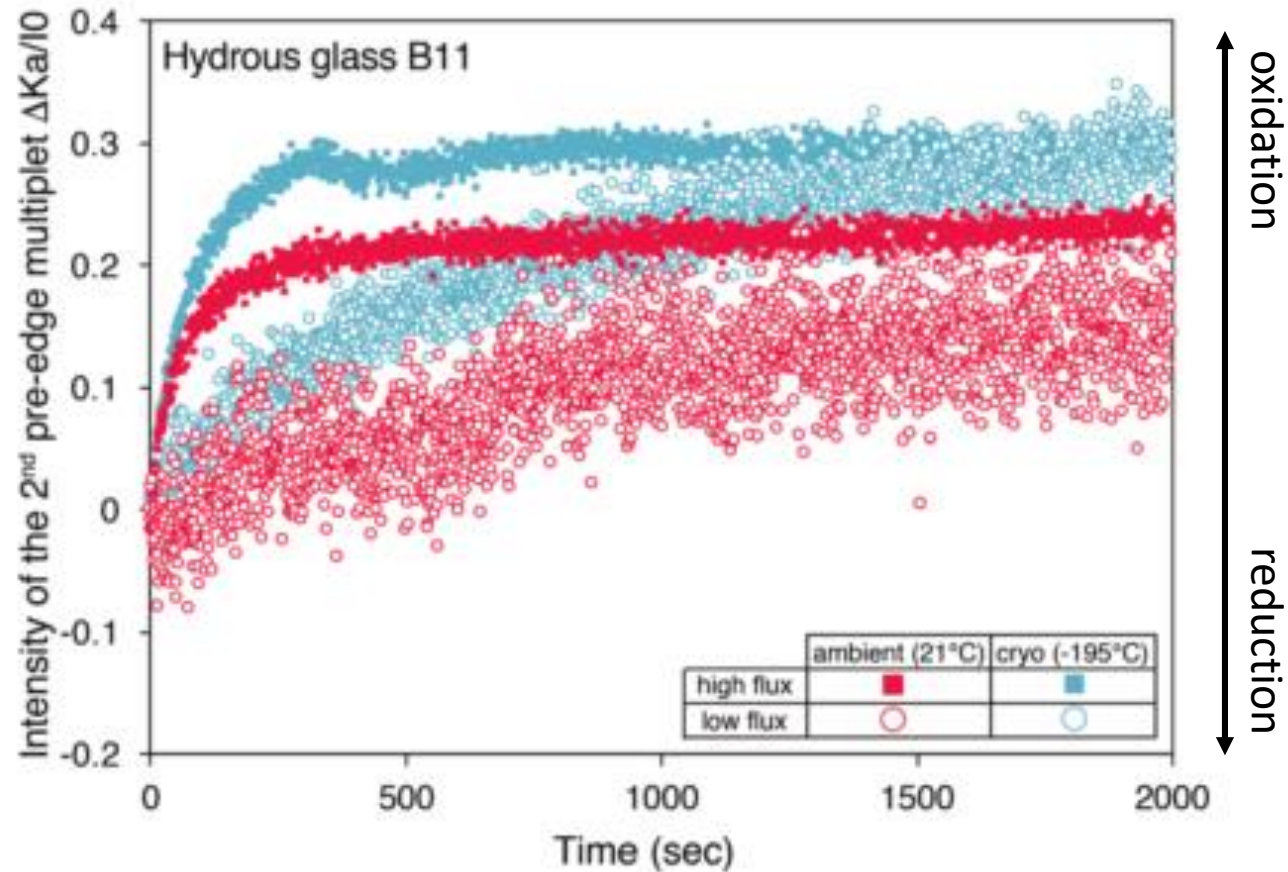
High Fe glass (5 wt% FeO): anhydrous  
basalts are stable, hydrous basalts oxidise



XANES damage

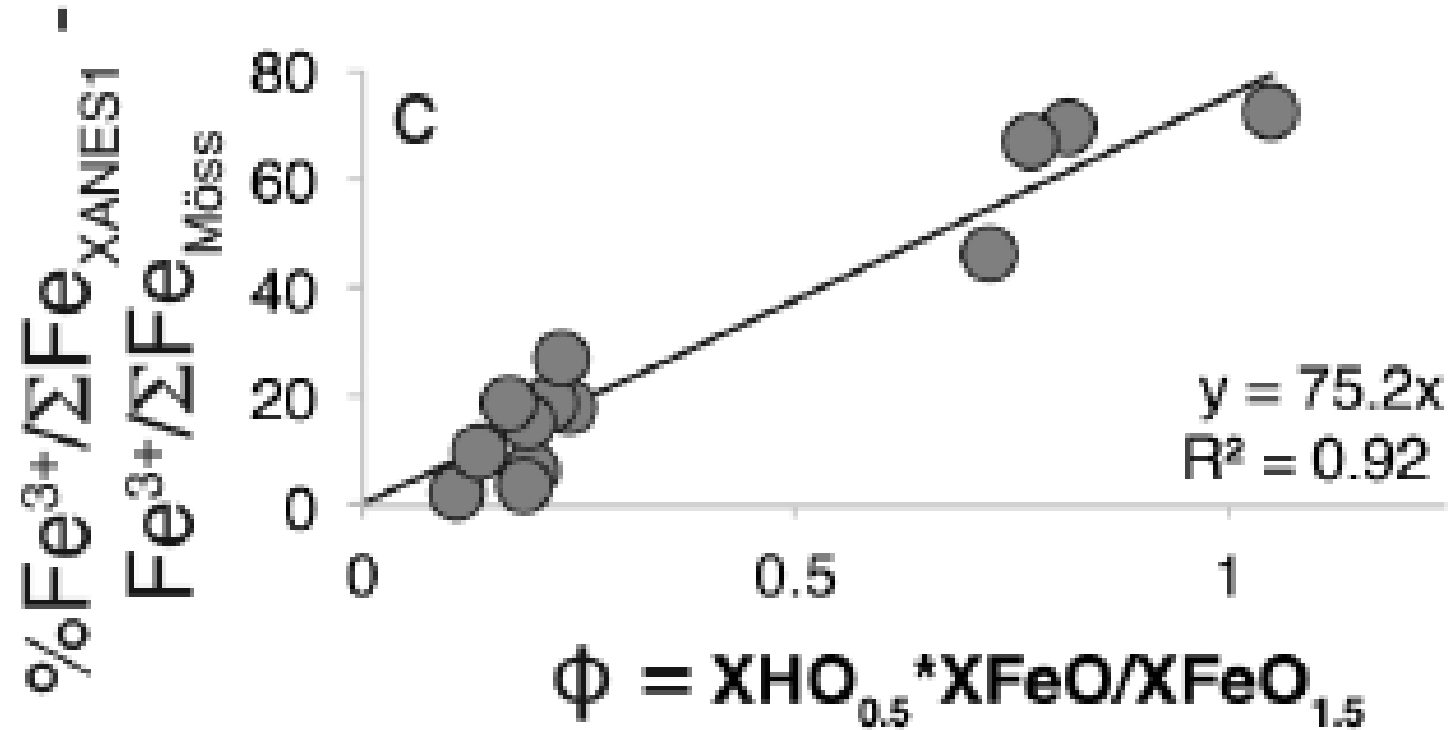
*Flux**Temperature*

Oxidation is exponential, increase photon flux increases rate of change, increased rate with decreased temperature



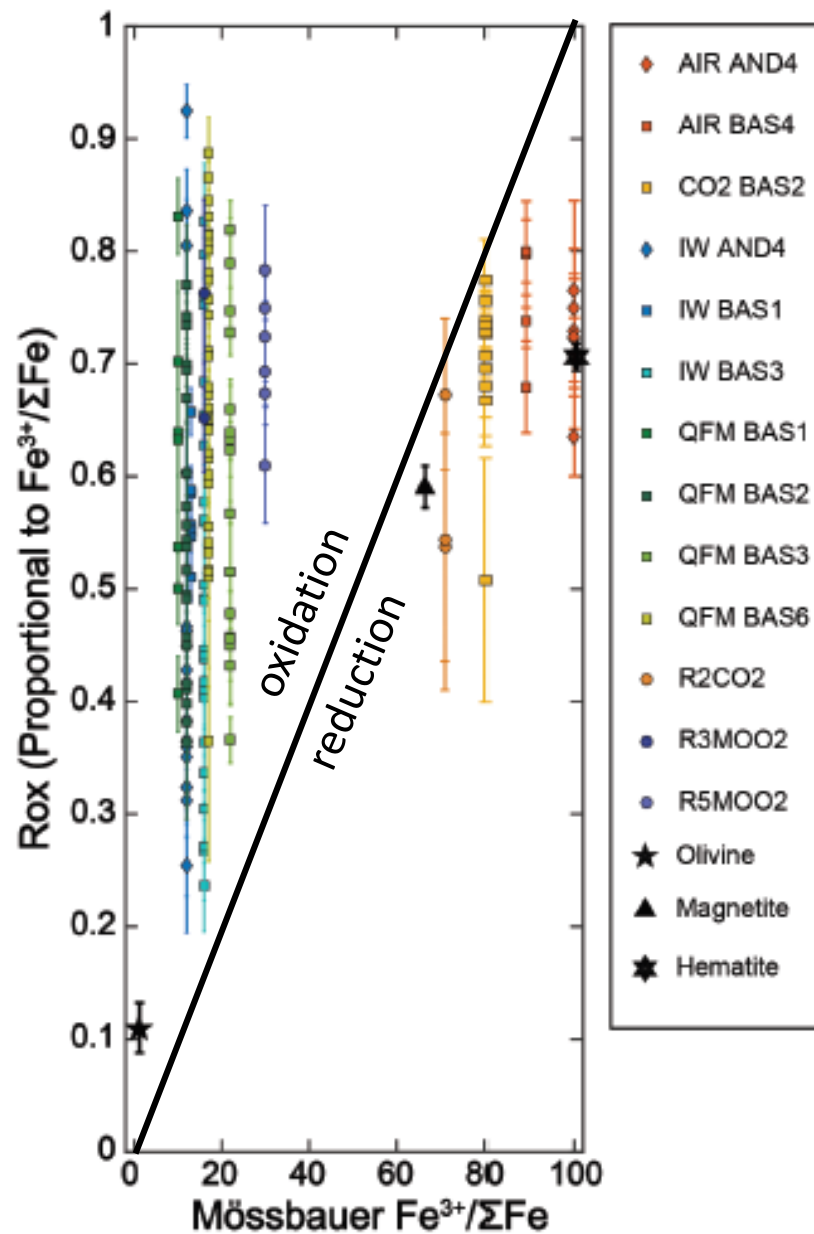
XANES damage  
*Composition*

Increased rate of oxidation with increased  
 $H_2O$  or reduced Fe concentration



## EELS damage

Both oxidation and  
reduction

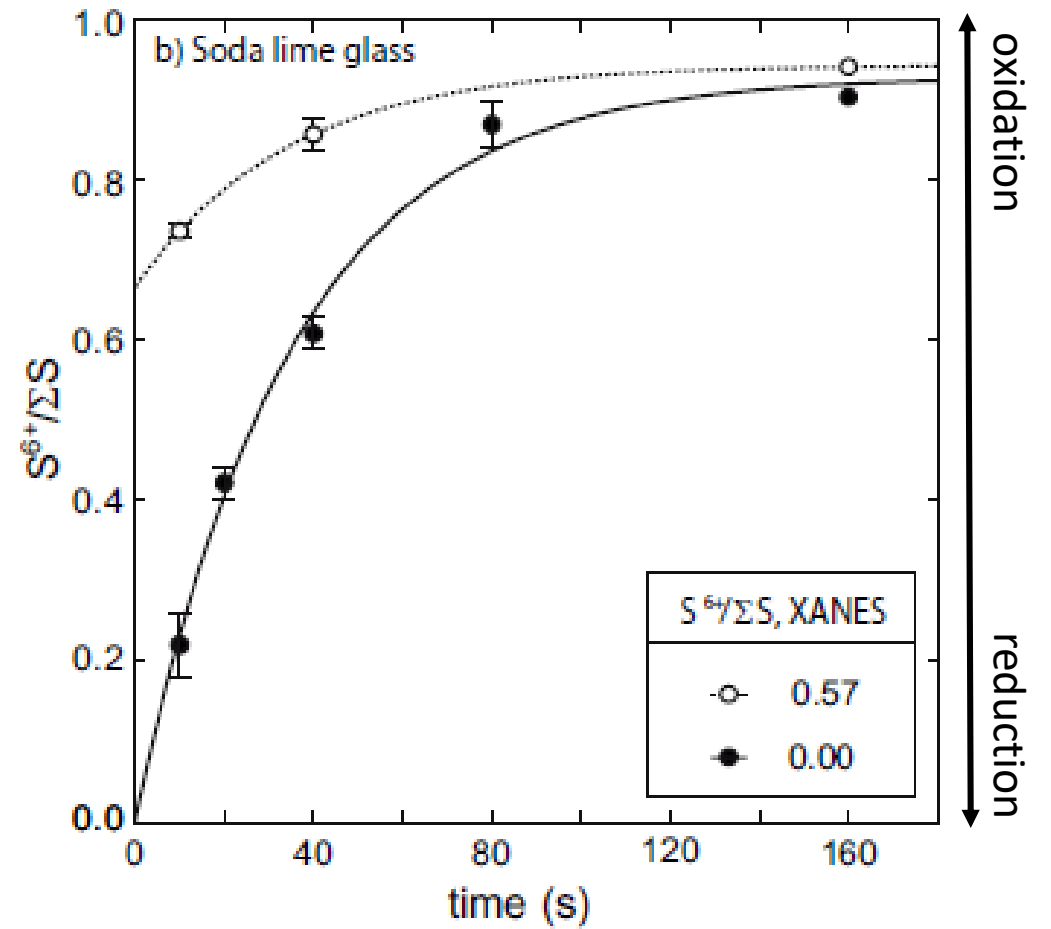
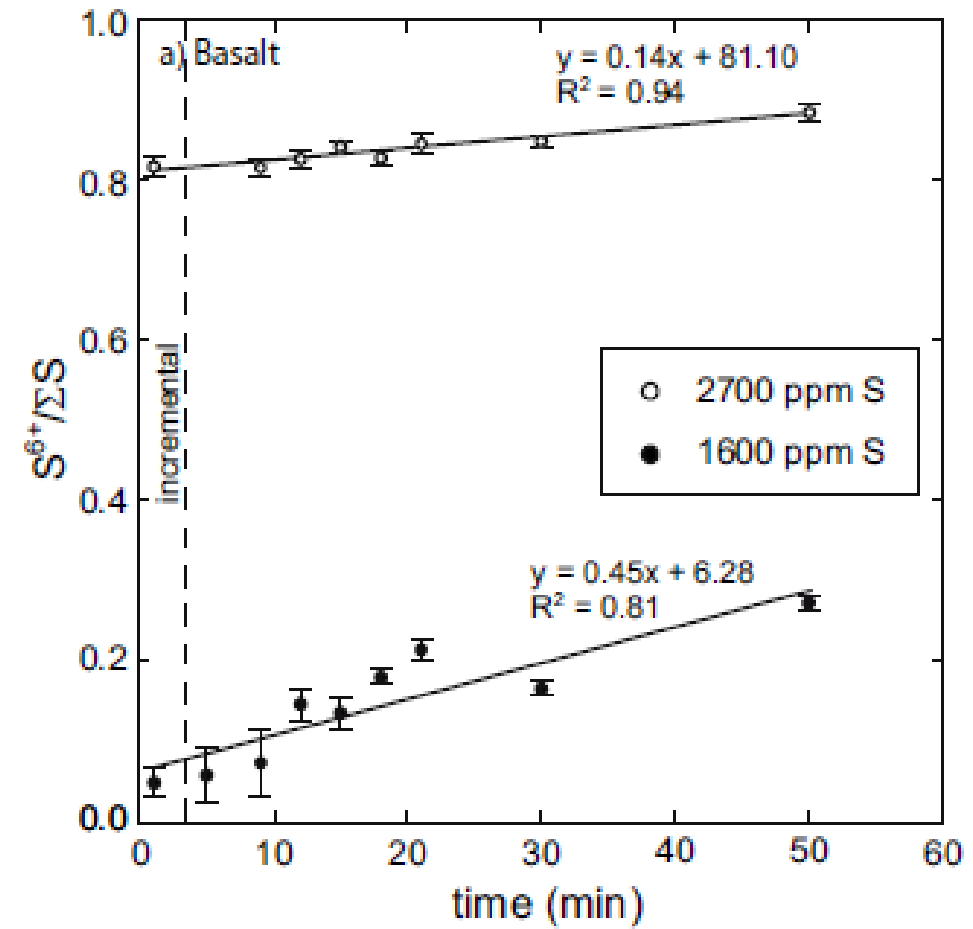


1. Mobile elements migrate
2. Fe oxidises and reduces depending on composition and analytical conditions
3. ... as does S

# EPMA damage

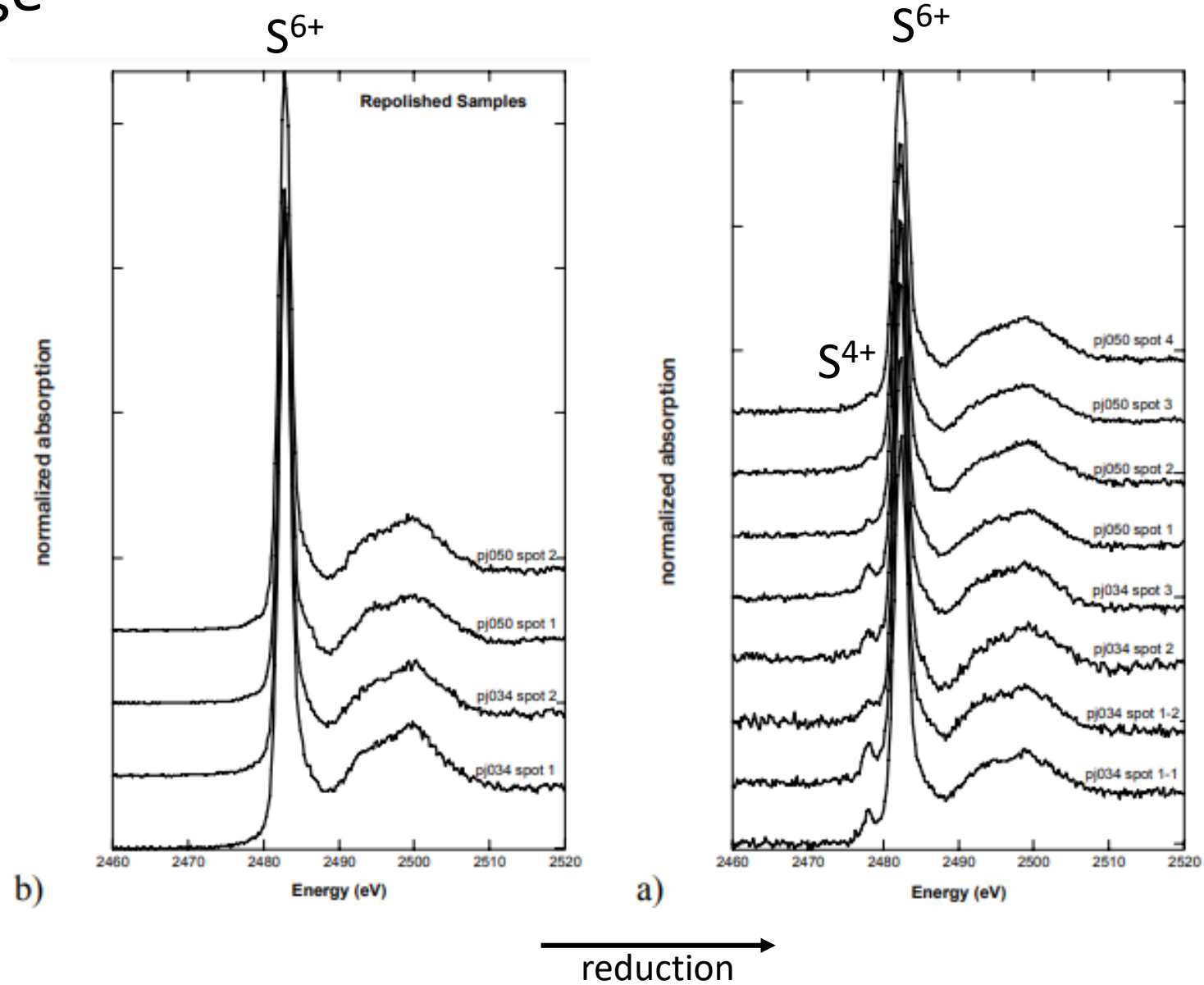
Composition: Fe content,  $S^{6+}/S_T$

More oxidation in low Fe glass, faster oxidation in initially reduced glass



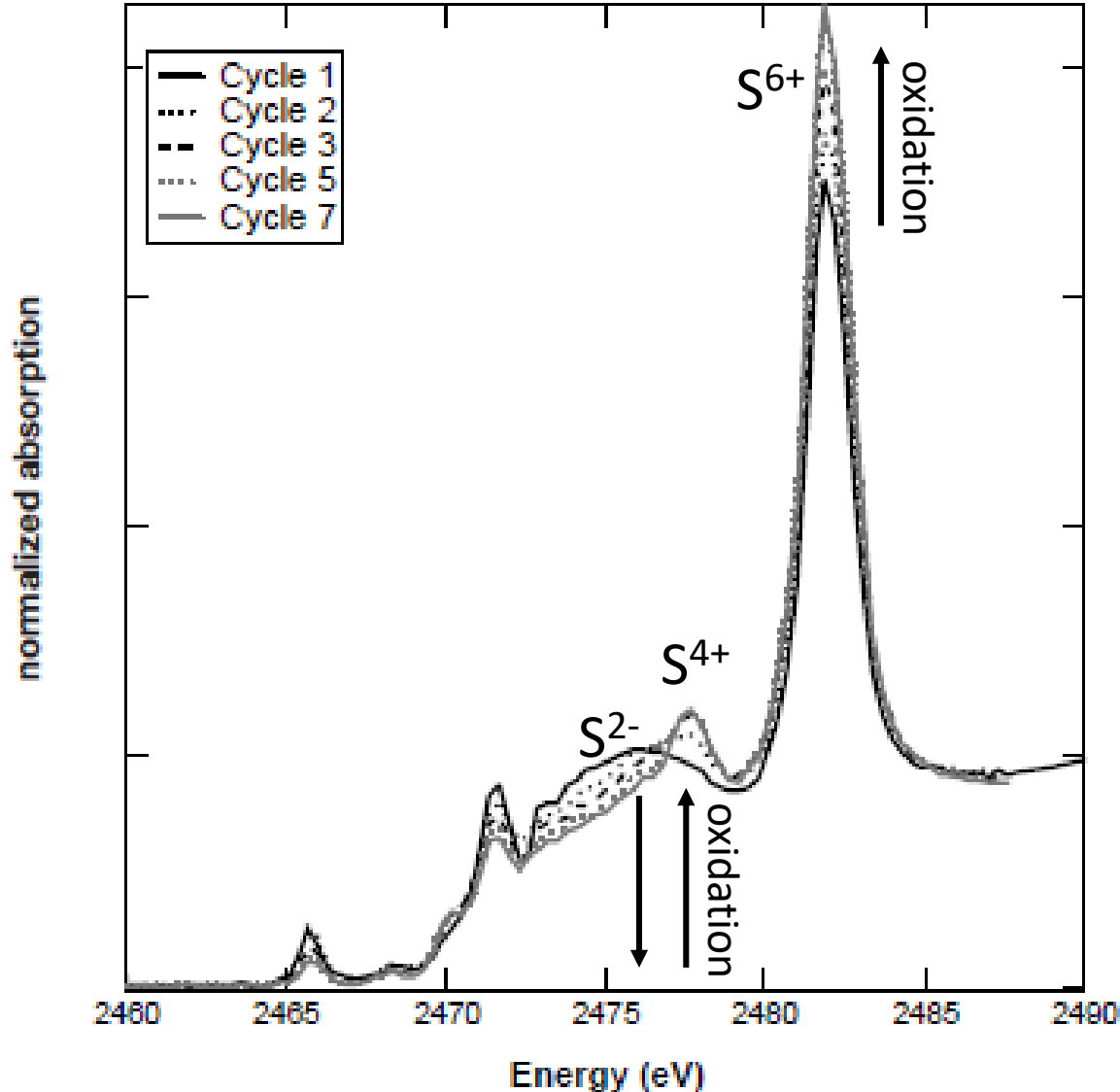
## EPMA damage

Reduction

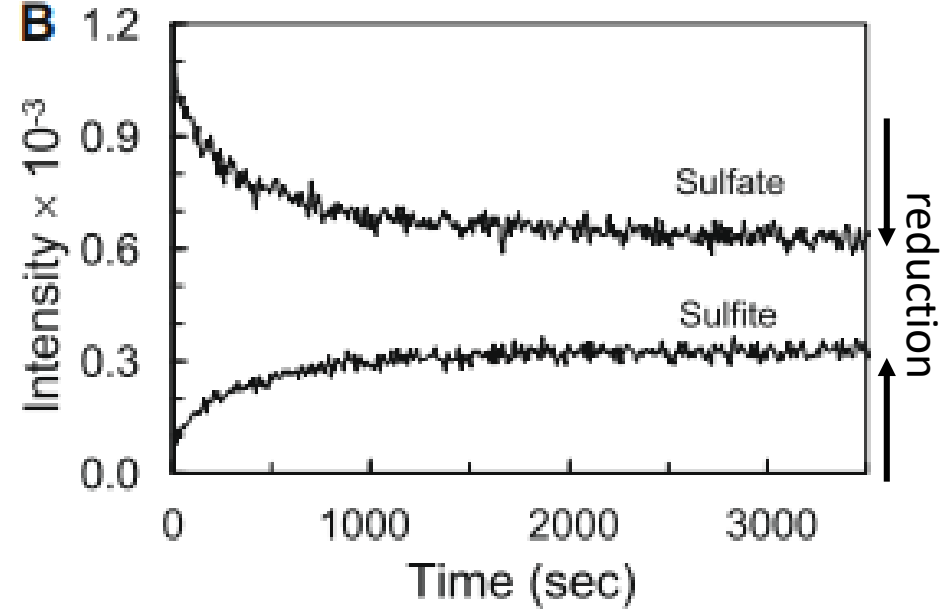
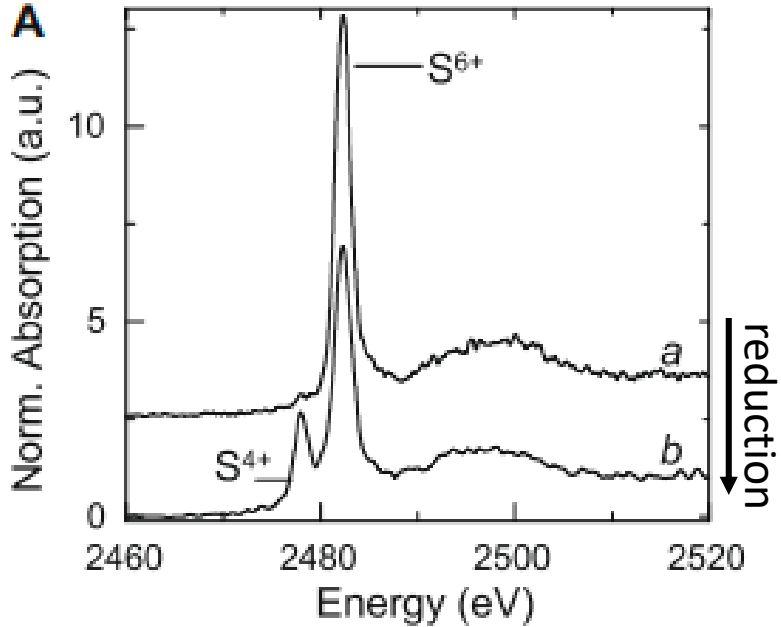
Presence of  $S^{4+}$  after irradiation

# XANES damage

Oxidation proceeds by  $S^{4+}$  formation

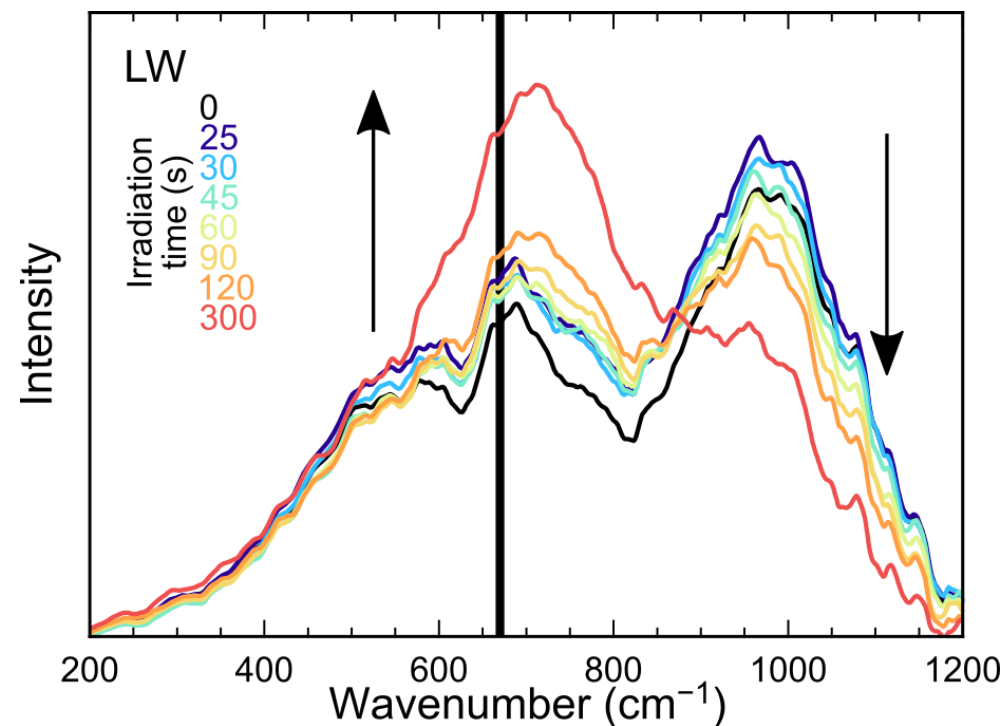
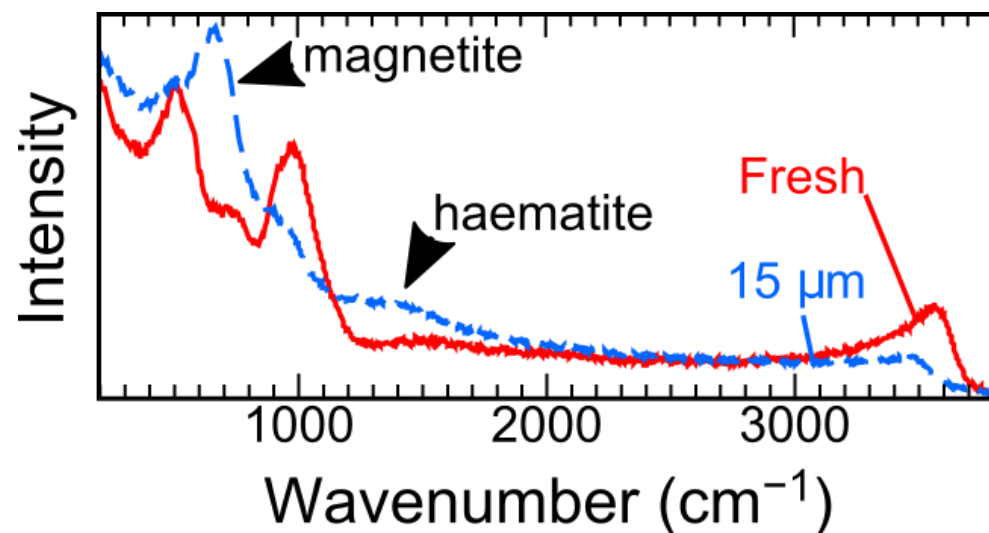


# XANES damage Reduction proceeds by S<sup>4+</sup> formation



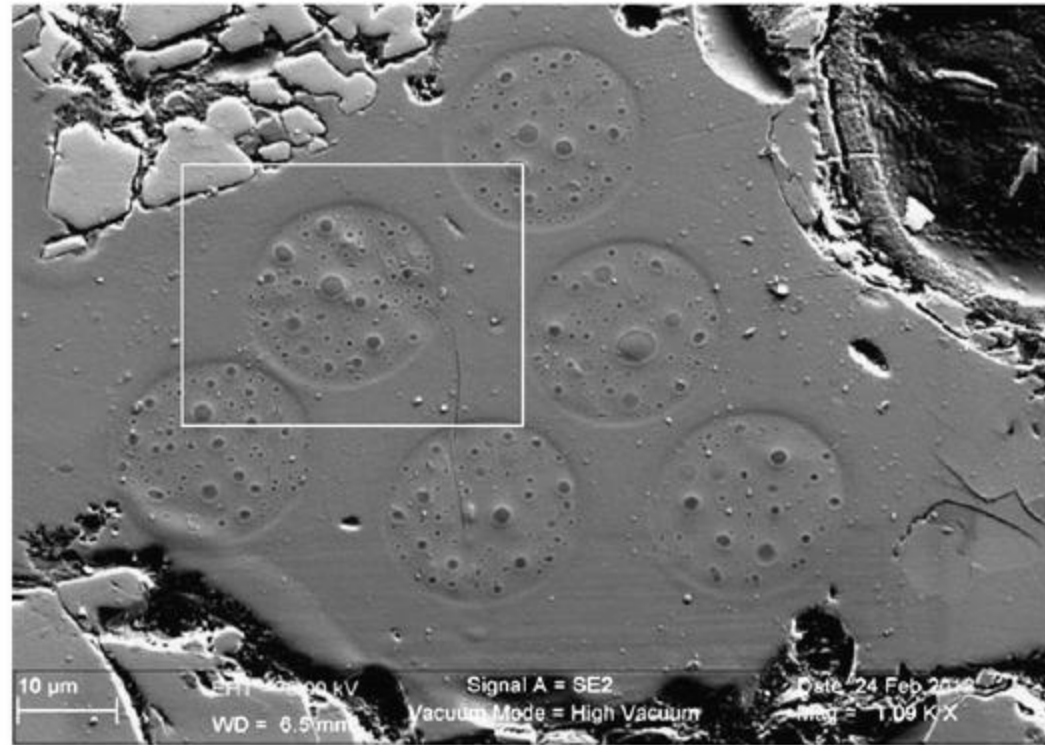
1. Mobile elements migrate
2. Fe oxidises and reduces depending on composition and analytical conditions
3. ... as does S
4. **Fe nanoparticles precipitate**

EPMA damage    Quantity of nanolites of magnetite (and haematite) increases with increasing beam damage

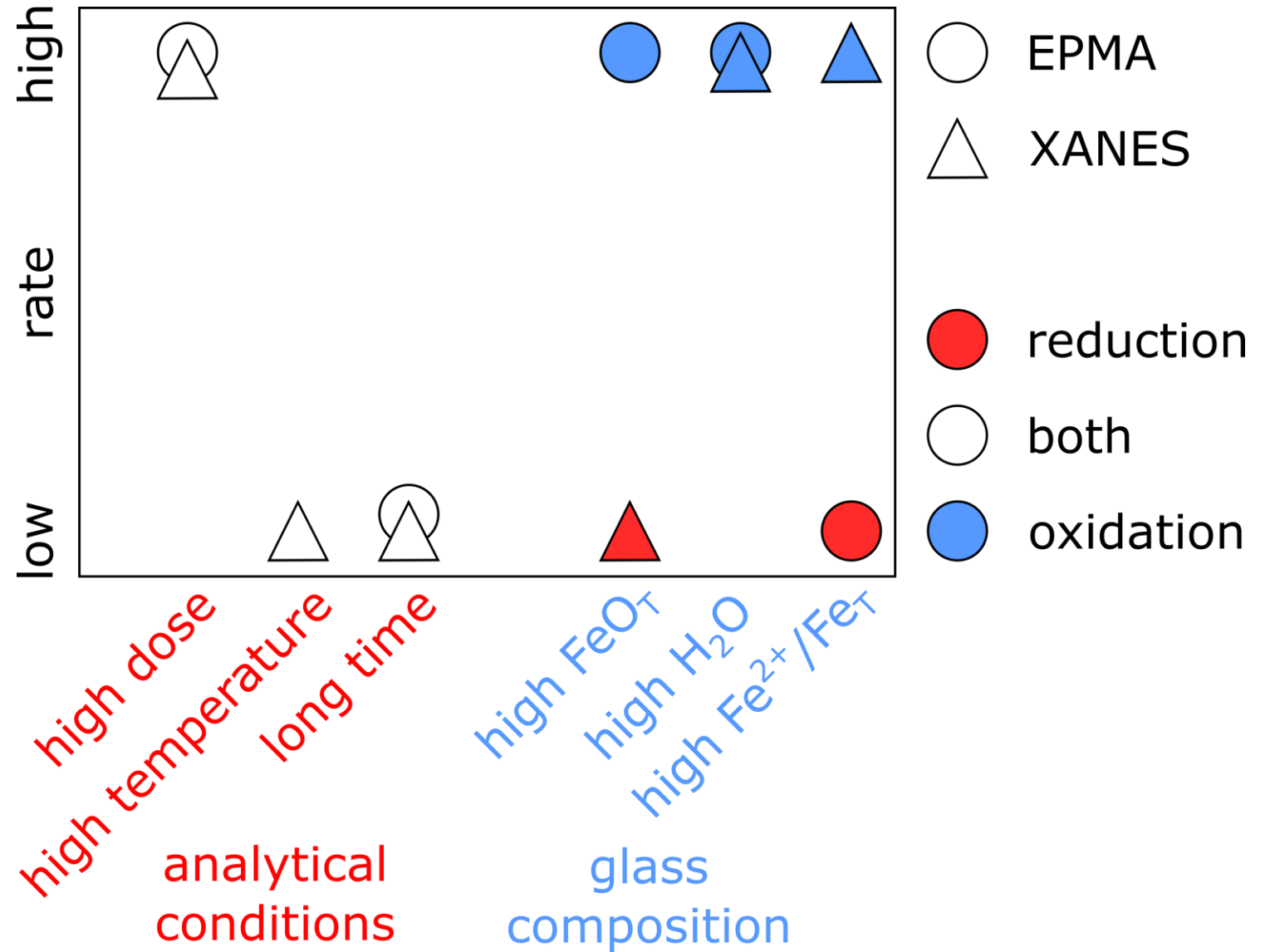


1. Mobile elements migrate
2. Fe oxidises and reduces depending on composition and analytical conditions
3. ... as does S
4. Fe nanoparticles precipitate
5. **Surface morphology changes**

EPMA damage Likely oxygen bubbles leaving the sample



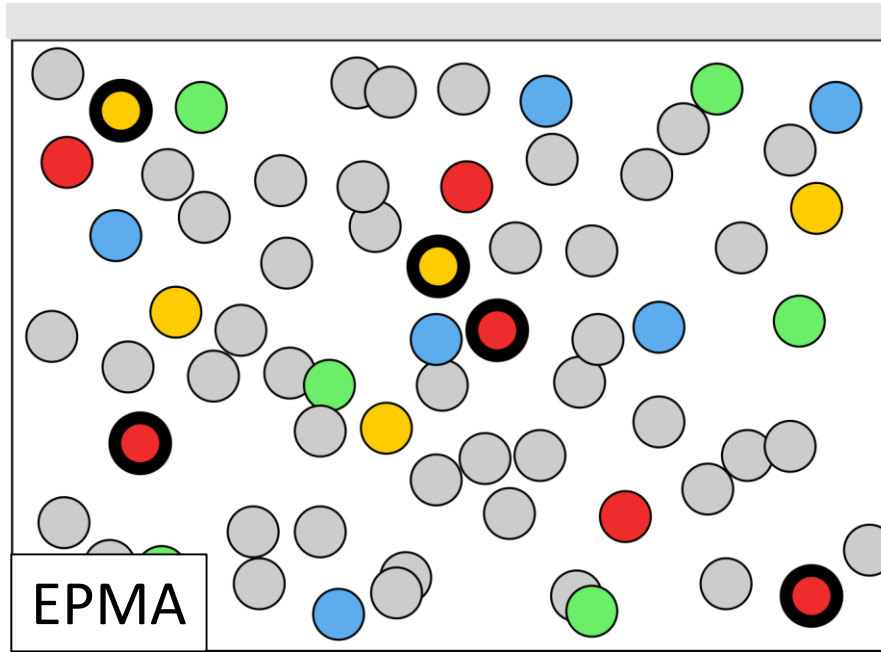
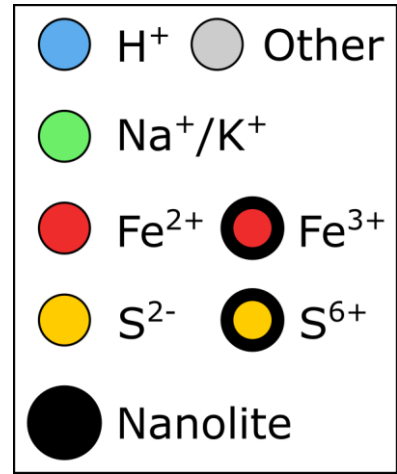
# Fe redox changes



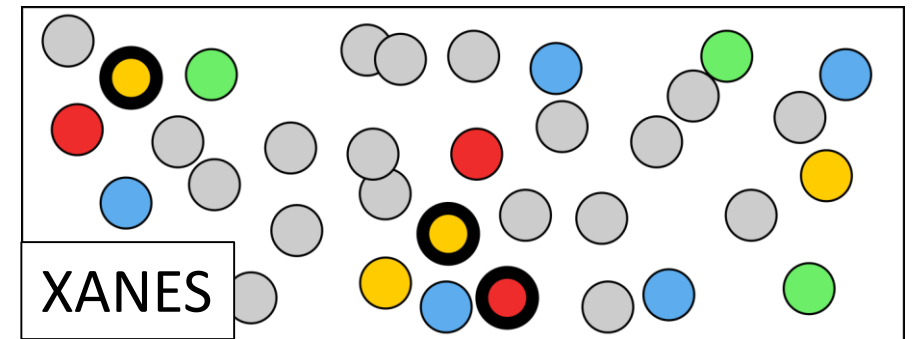
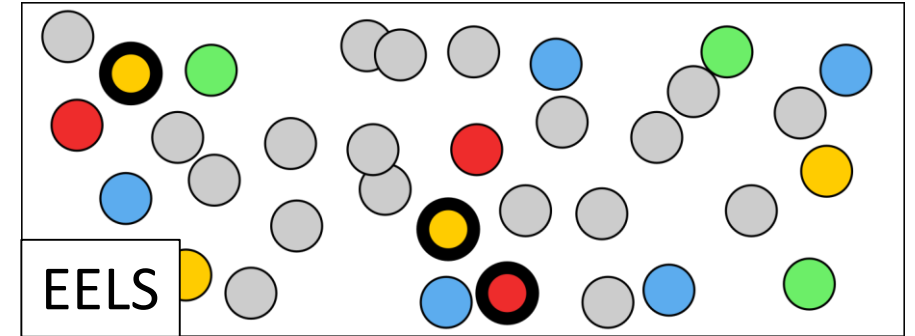
# Mechanisms

# Pre-irradiation

thick sample, carbon coated

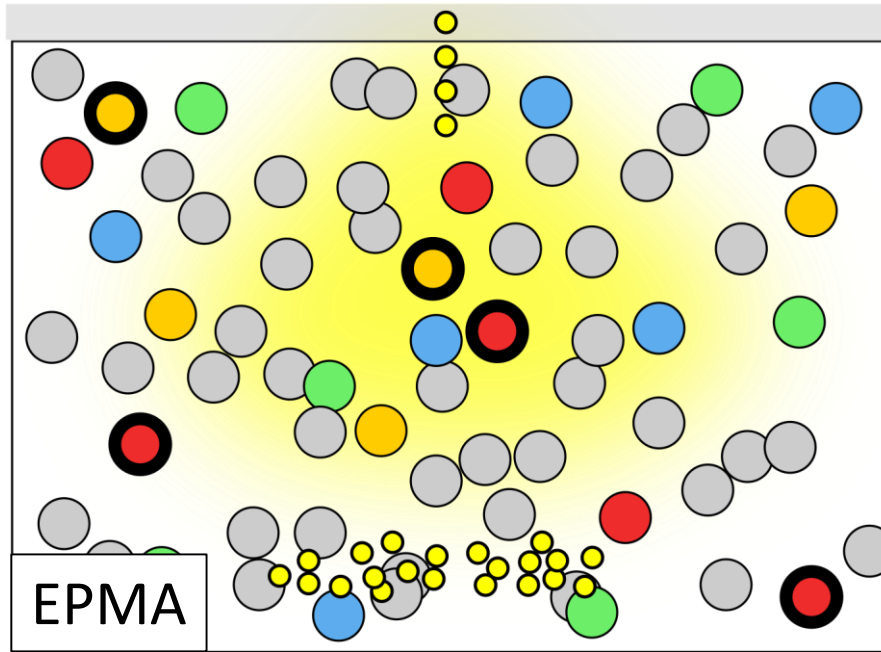
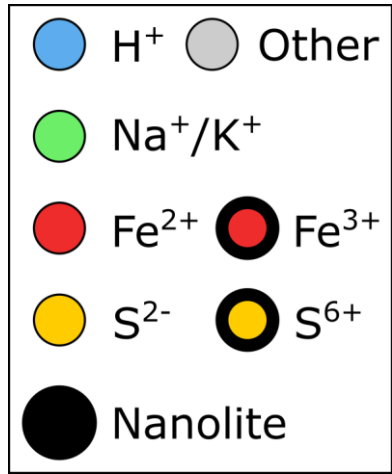


Transmission techniques therefore thin samples



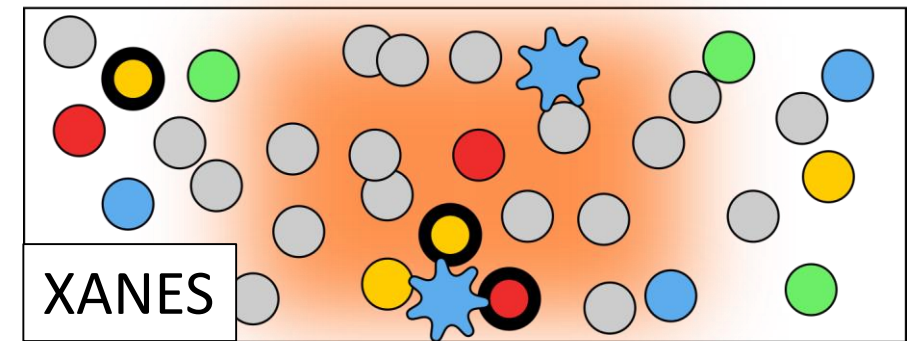
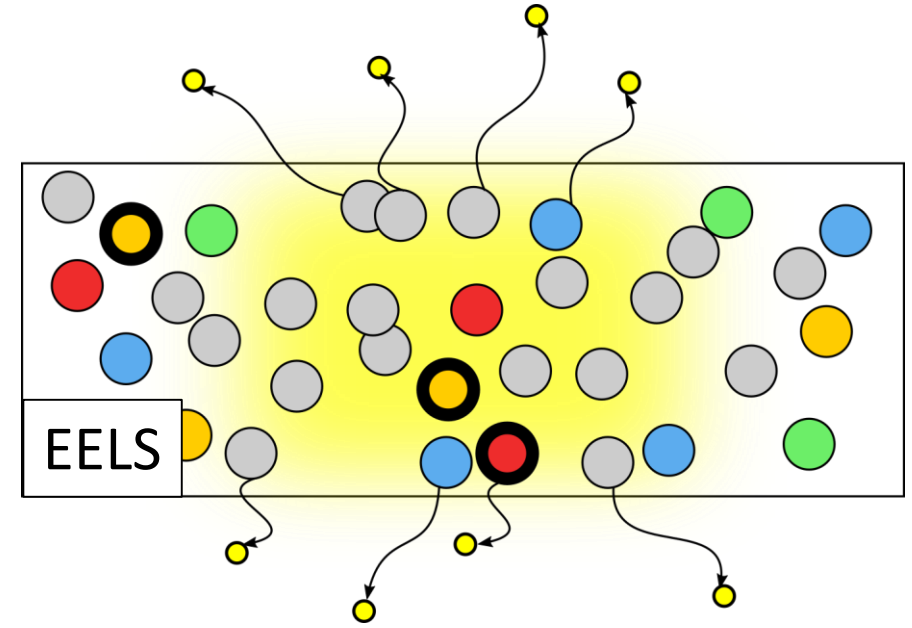
**Beam on**

EPMA: glass is an insulator so traps electrons causing sub-surface charging (no surface charging due to carbon coat)



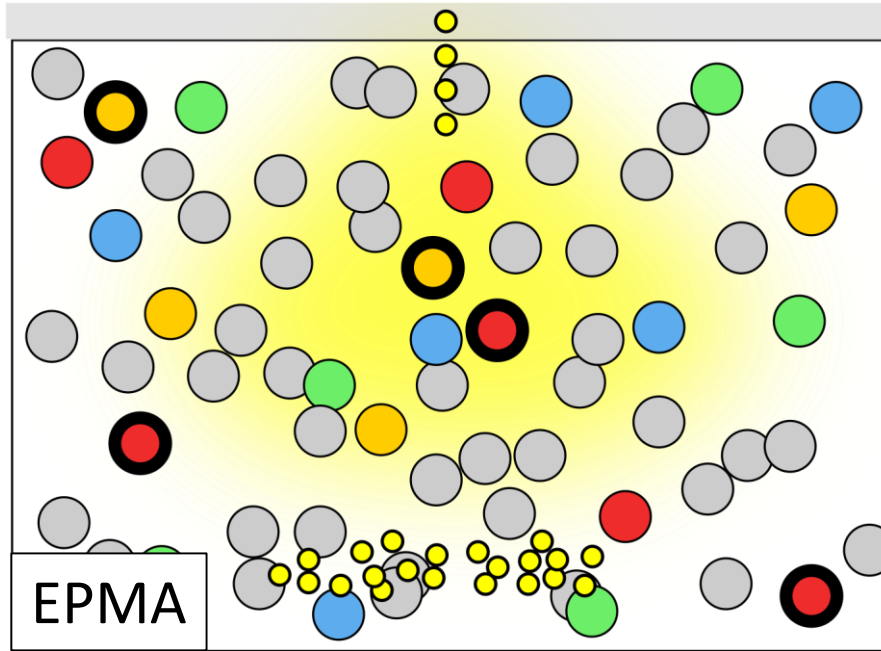
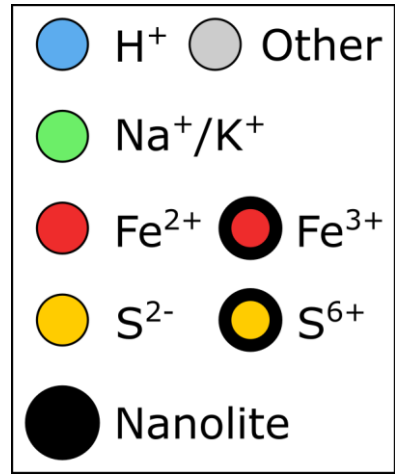
$e^-$  trapping generates negative charge

Cazaux (1996) *X-ray spec.* 25(6)265-280



**Beam on**

EELS: thin sample so significant secondary electron emission

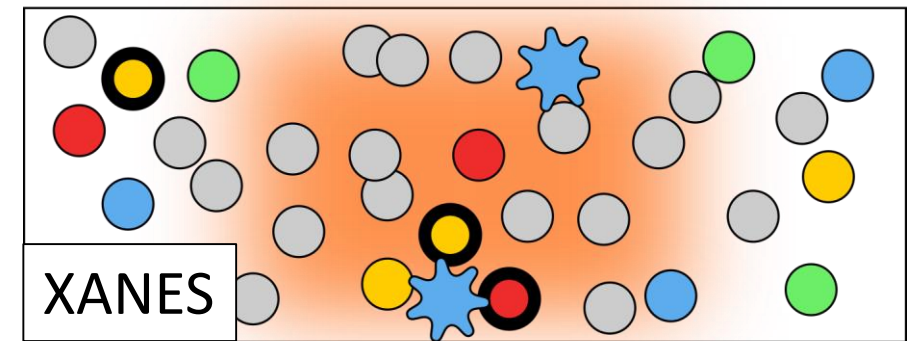
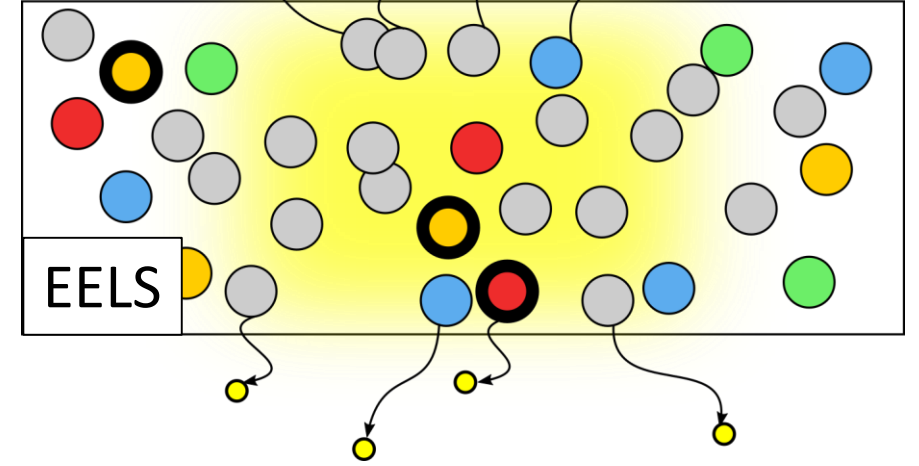


$e^-$  trapping generates negative charge

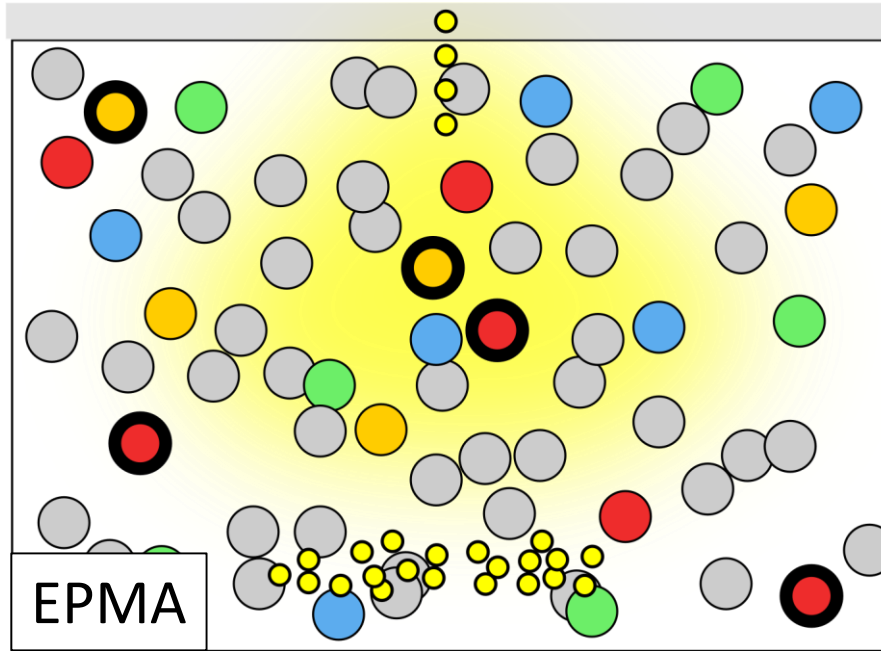
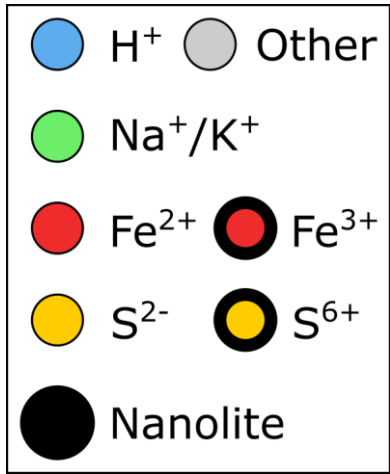
Cazaux (1996) *X-ray spec.* 25(6)265-280

2° e- emission generates positive charge

Jiang (2013)  
*J. App. Phys.*  
46(3):305502



# Beam on

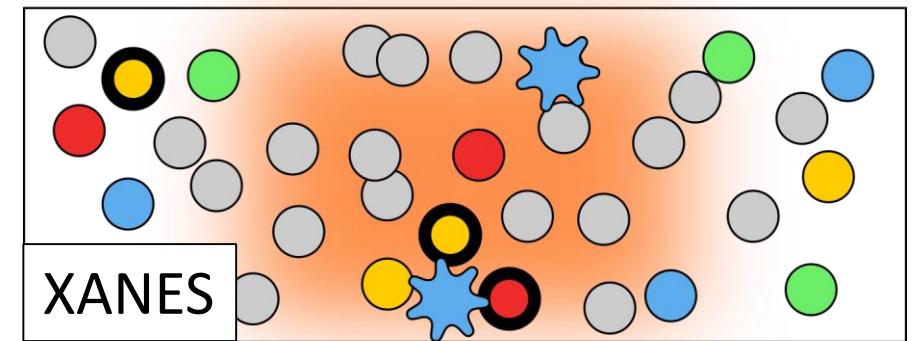
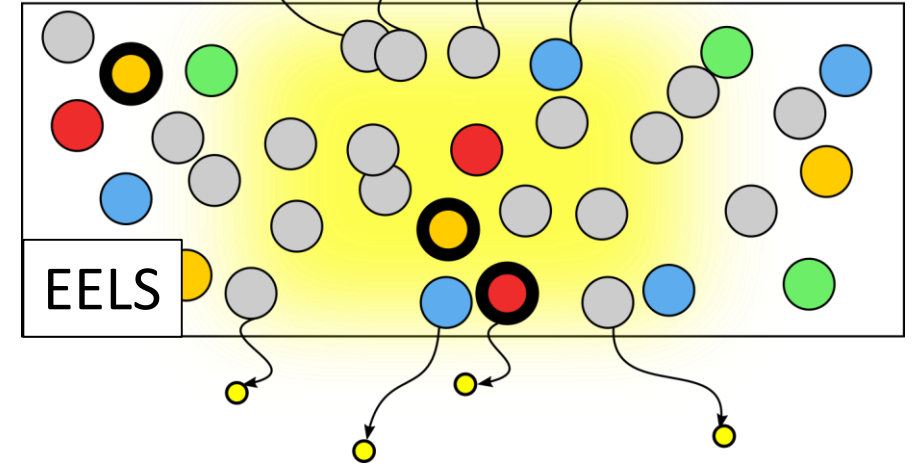


$e^-$  trapping generates  
negative charge

Cazaux (1996) *X-ray spec.* 25(6)265-280

2° e- emission generates  
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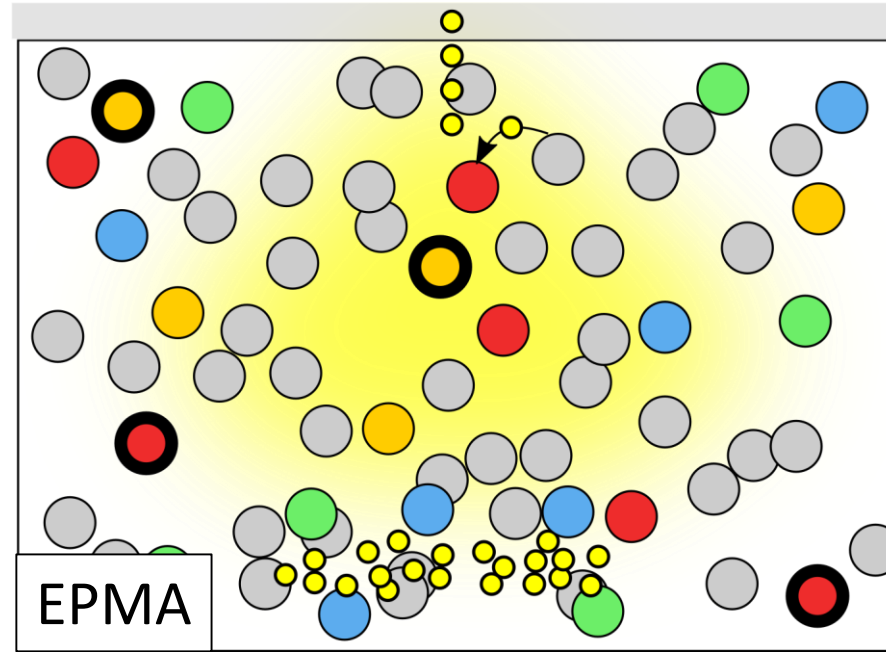
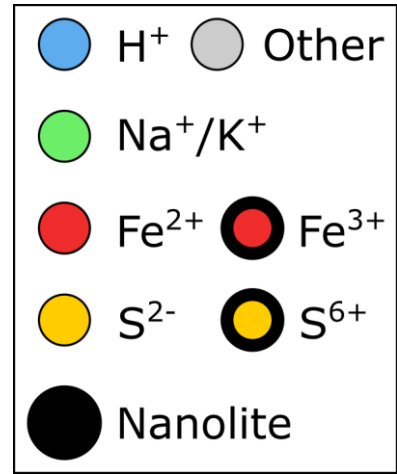


incident ionising radiation  
breaks O-H bonds

Cottrell *et al.* (2018) *Am. Min.* 103: 489-501

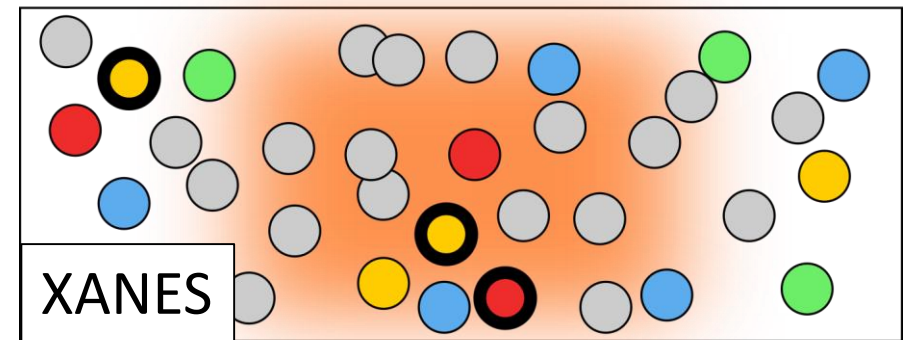
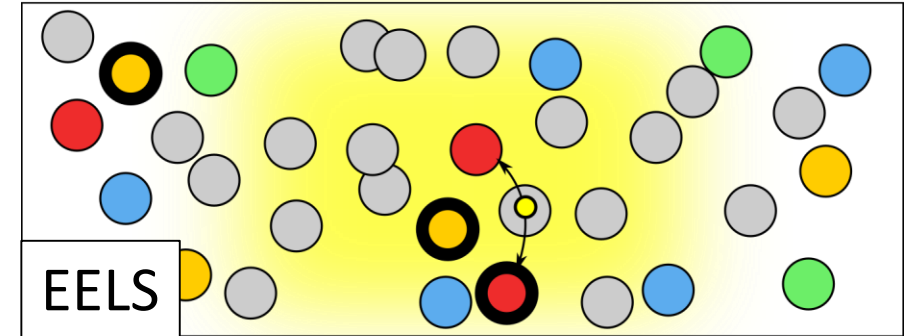
# Fe reduction

EPMA: stable if already reduced, reduction always occurring but sometimes overtaken by oxidation



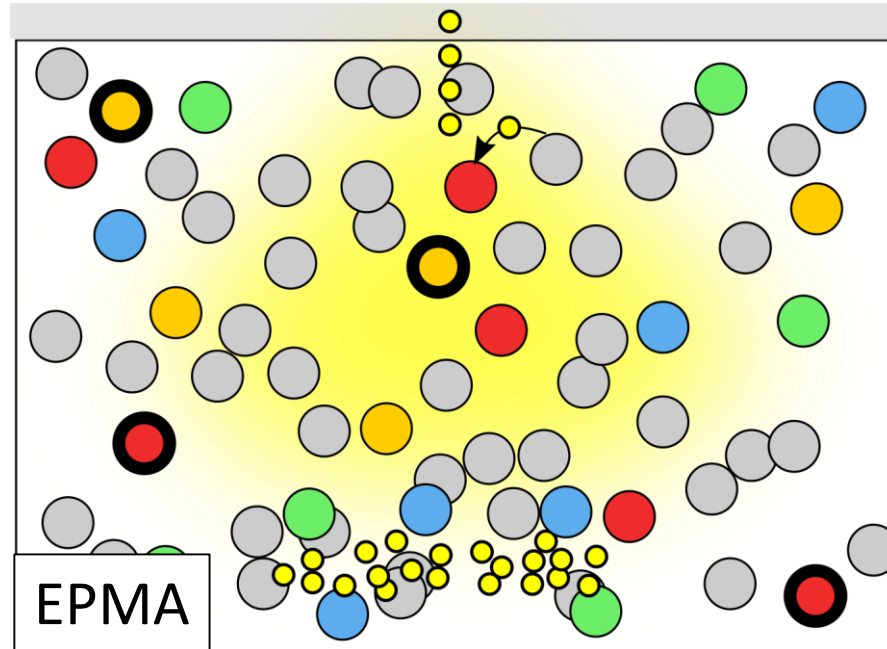
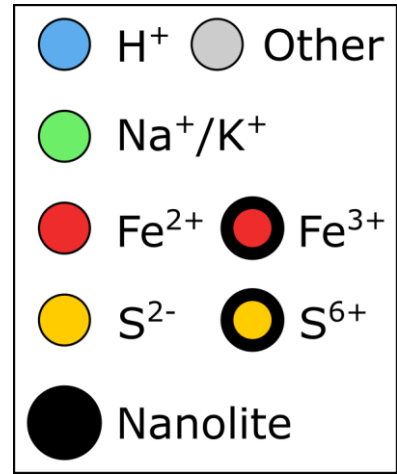
$e^-$  transfer from O to  $Fe^{3+}$  if initially oxidised

Nishida (1995) *Hyp. Int.* 95(1):23-29



# Fe reduction

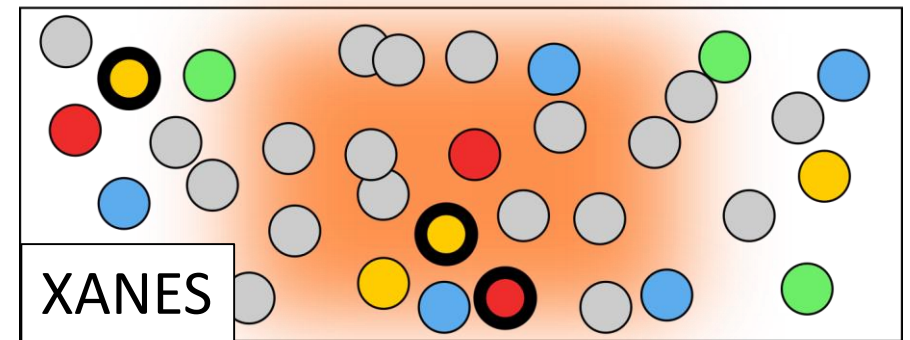
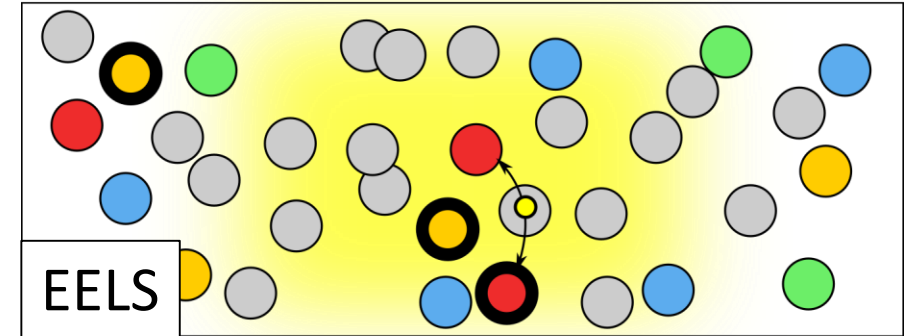
EELS: semiconductive-nature allows electron hopping



$e^-$  transfer from O to  $Fe^{3+}$  if initially oxidised

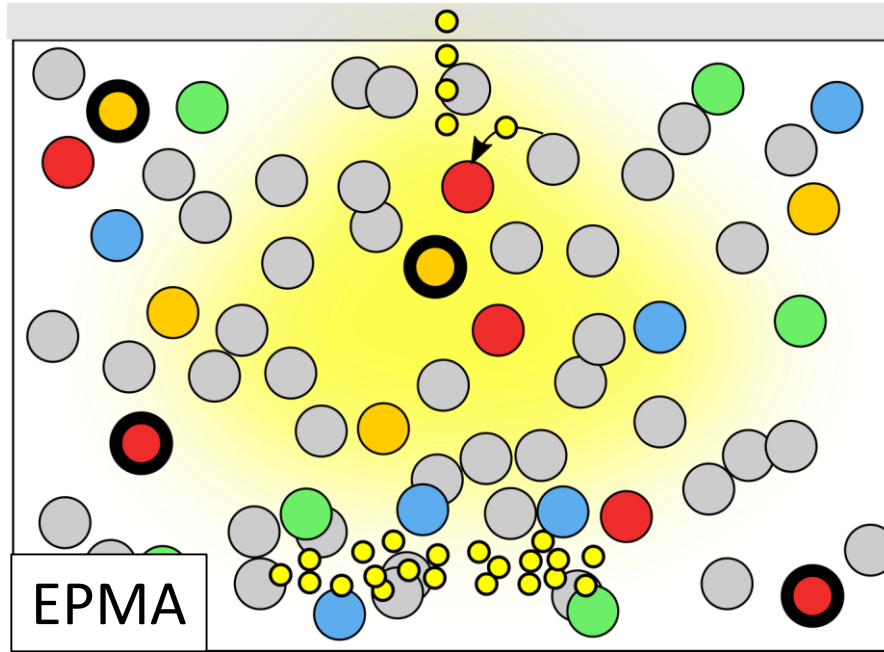
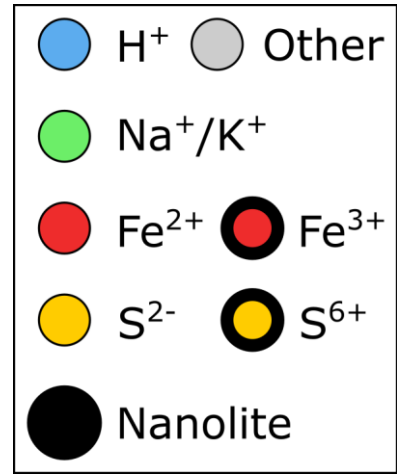
Nishida (1995) *Hyp. Int.* 95(1):23-29

$e^-$  hop between  $Fe^{2+}$  &  $Fe^{3+}$   
Burgess *et al.* (2016) *Am. Min.* 101(12): 2677-2688



# Fe reduction

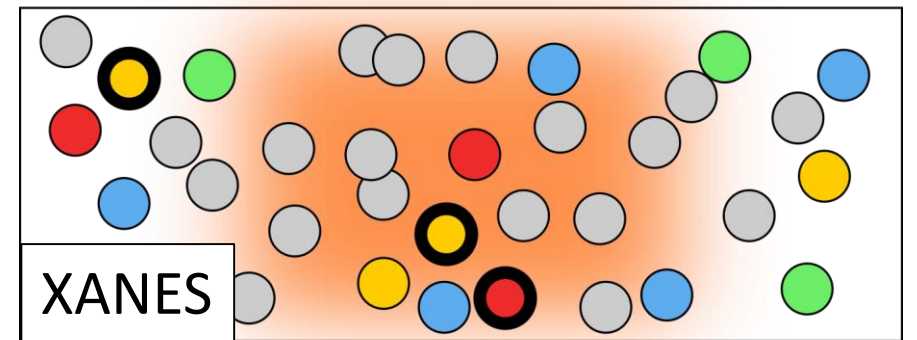
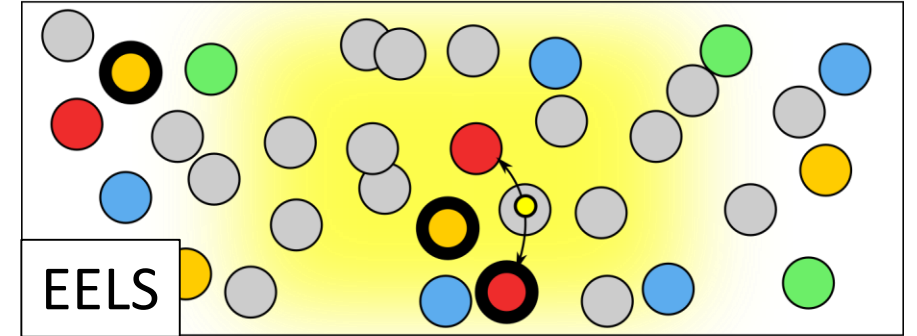
XANES: defects relax at high temperature



$e^-$  transfer from O to  $Fe^{3+}$  if initially oxidised

Nishida (1995) *Hyp. Int.* 95(1):23-29

$e^-$  hop between  $Fe^{2+}$  &  $Fe^{3+}$   
Burgess *et al.* (2016) *Am. Min.* 101(12): 2677-2688

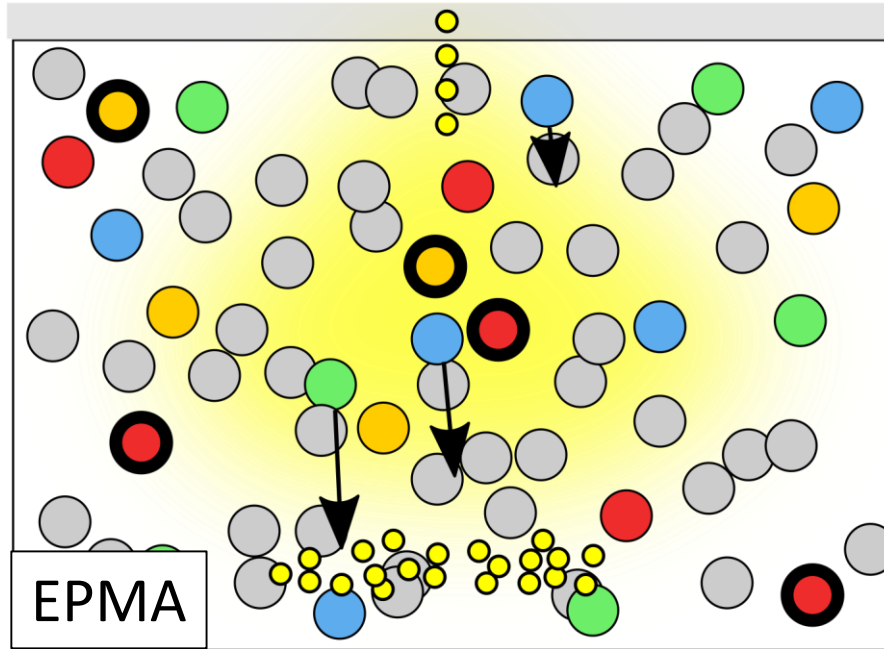
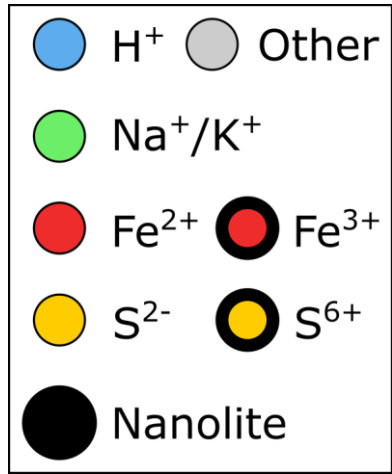


creation of localise charge defects providing charges to  $Fe^{3+}$

Gonçalves Ferreira *et al.* (2013) *Chem. Geo.* 346:106-112

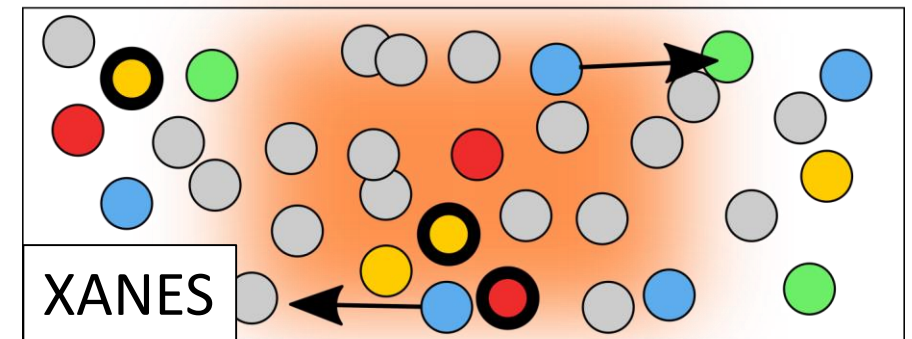
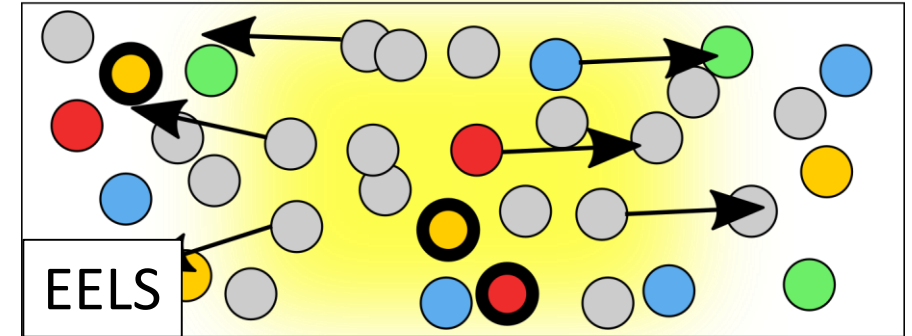
# Migration

EPMA: hydrous glass – alkali/H<sub>2</sub>O migration, leaves O behind which can outgas

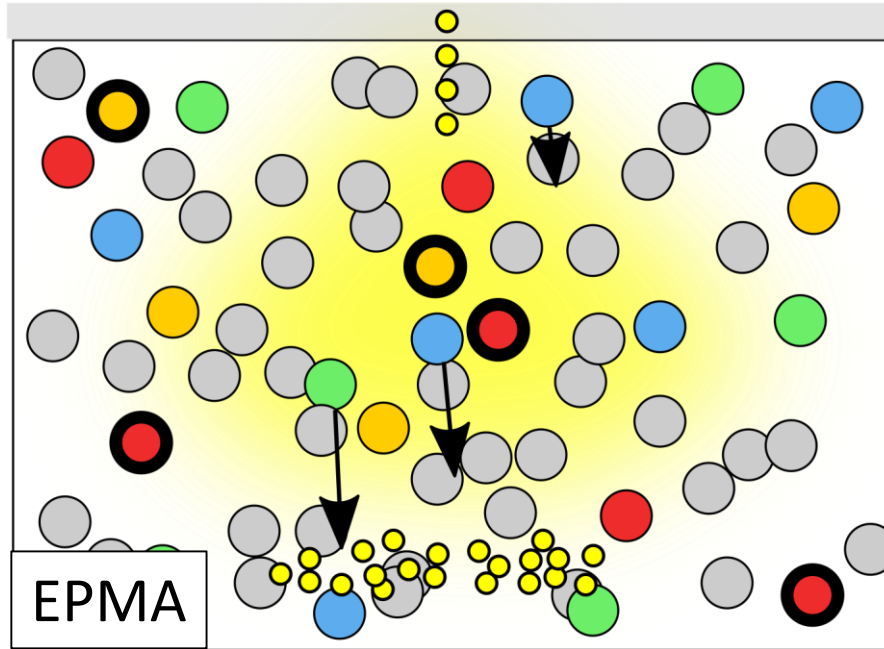
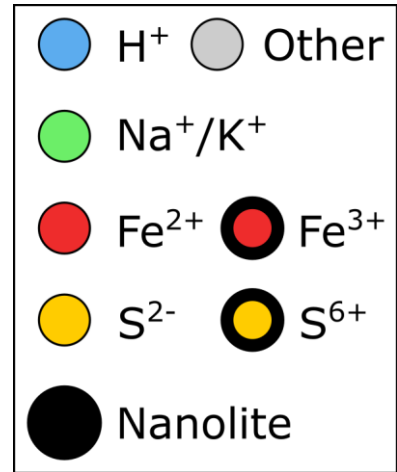


mobile elements migrate towards negative charge

Humphreys *et al.* (2006) *Am. Min.* 91(6): 667-679



# Migration

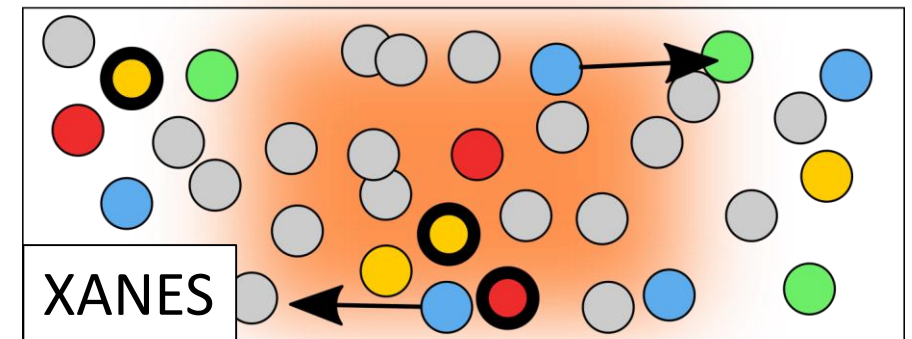
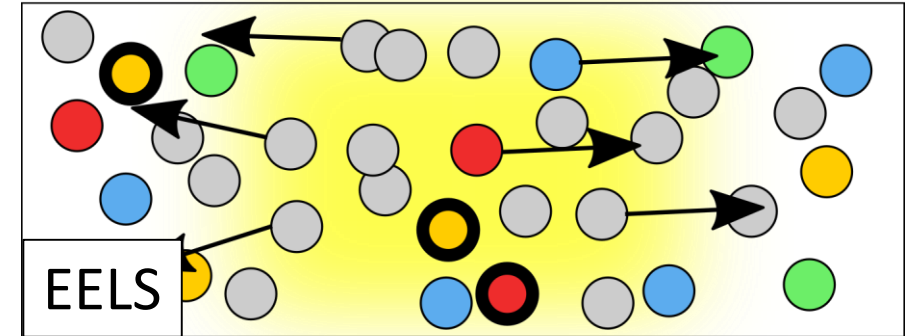


mobile elements migrate towards negative charge

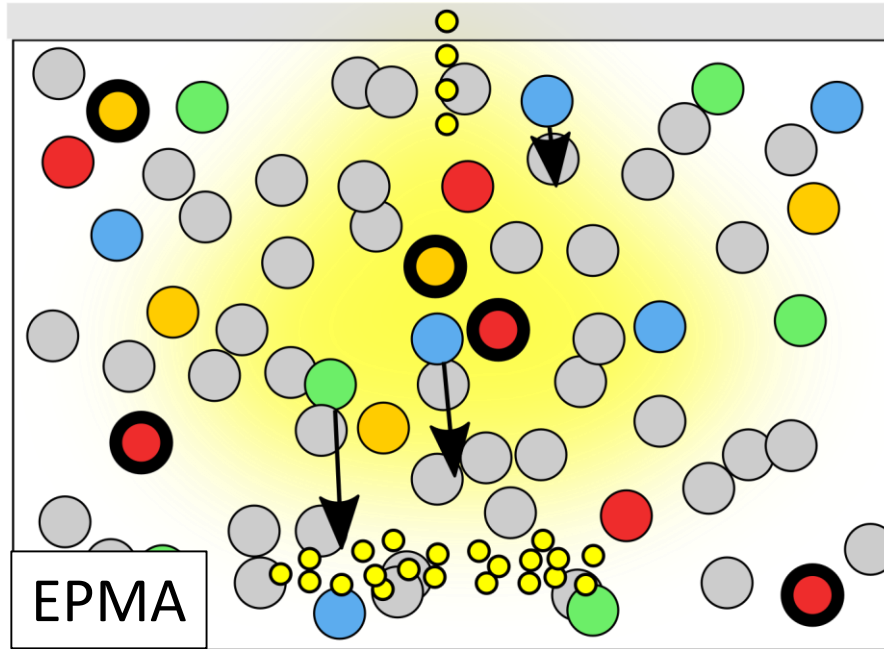
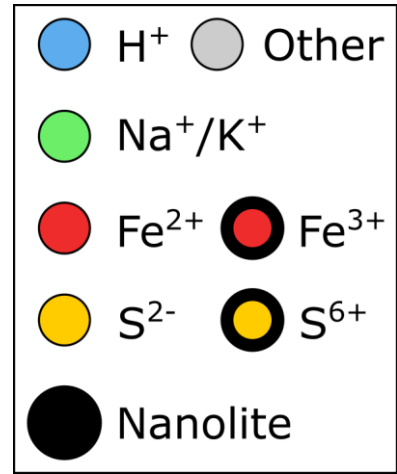
Humphreys *et al.* (2006) *Am. Min.* 91(6): 667-679

most elements migrate away from positive charge

Burgess *et al.* (2016) *Am. Min.* 101(12): 2677-2688



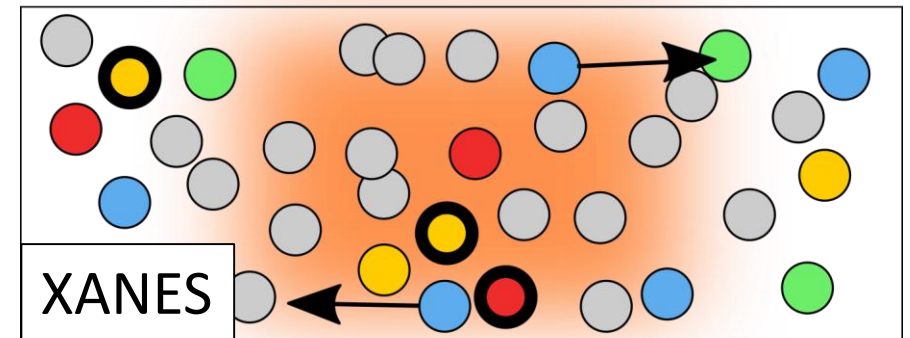
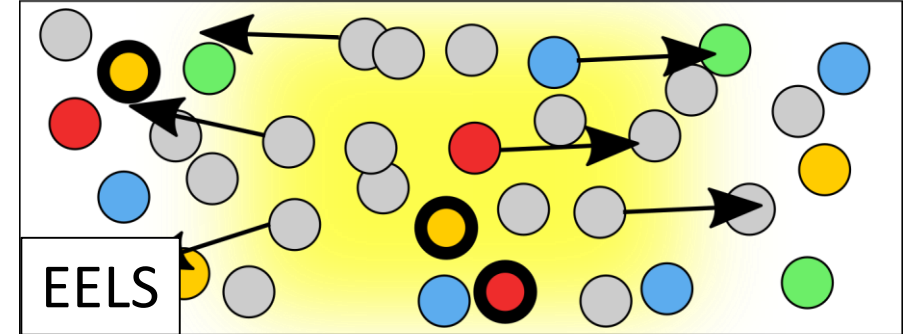
# Migration



mobile elements migrate towards negative charge

Humphreys *et al.* (2006) *Am. Min.* 91(6): 667-679

most elements migrate away from positive charge  
 Burgess *et al.* (2016) *Am. Min.* 101(12): 2677-2688

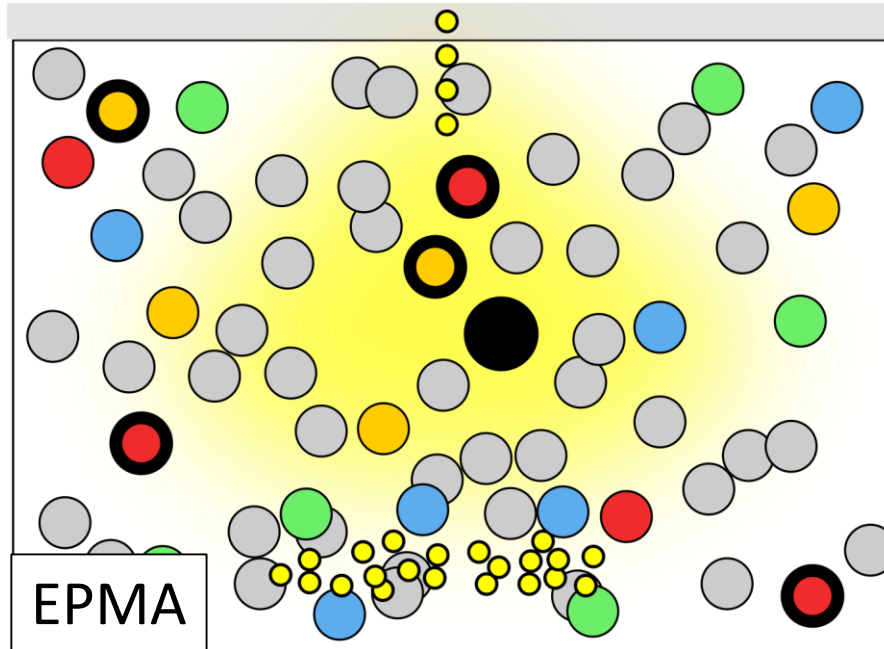
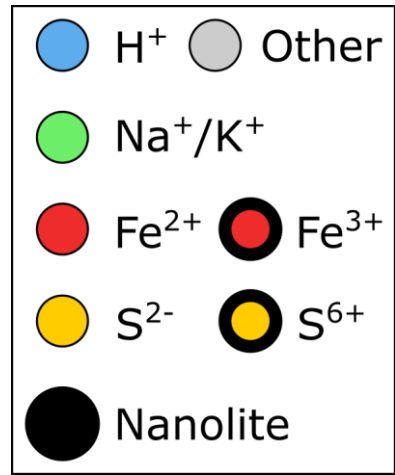


**H migrates quicker than O**

Cottrell *et al.* (2018) *Am. Min.* 103: 489-501

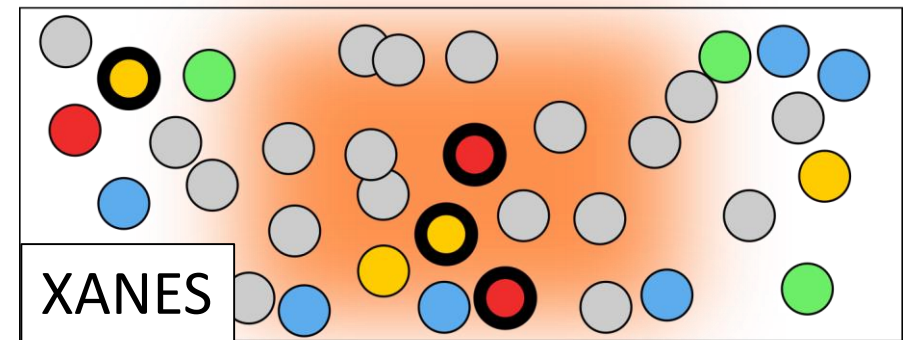
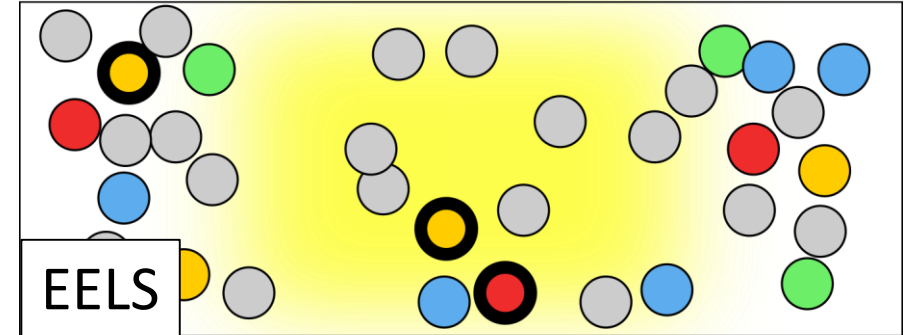
# Fe oxidation

EPMA: stable if low Fe

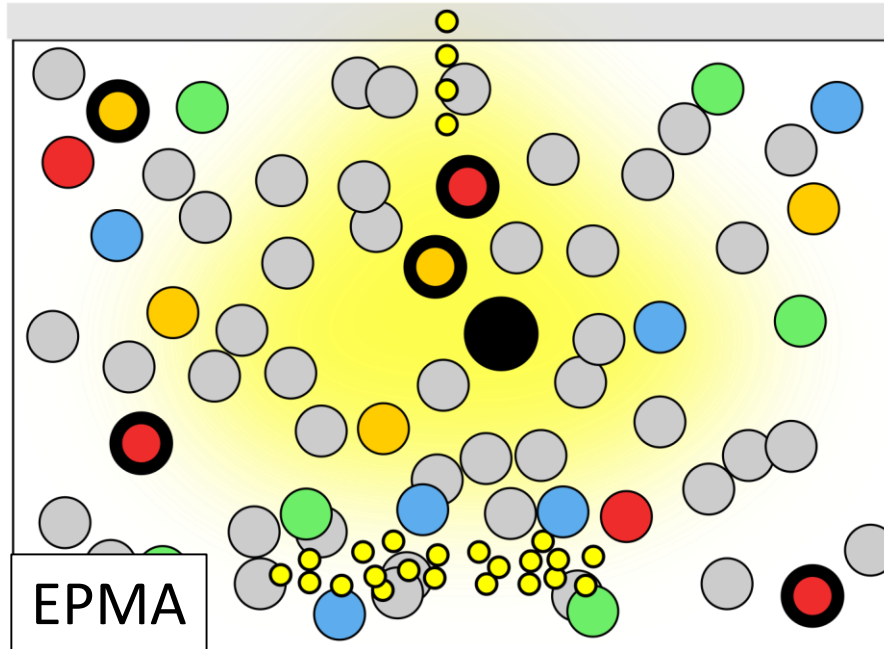
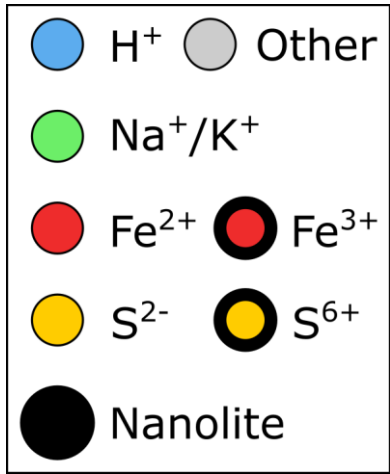


If high Fe, oxidation by precipitating mag/haem

Hughes *et al.* (2018) *Am. Min.* 103:1445-1454



# Fe oxidation

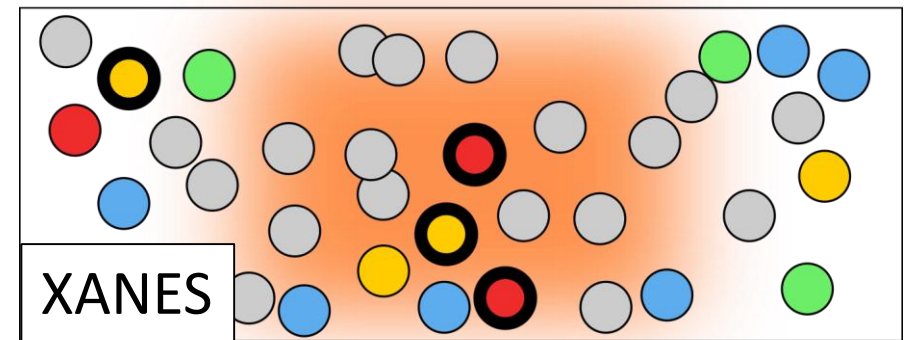
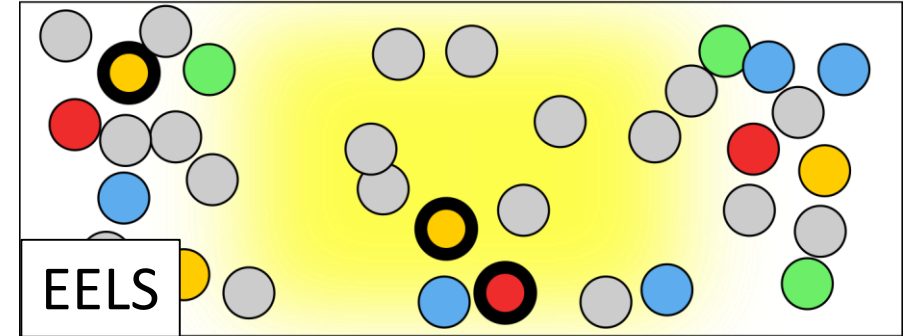


If high Fe, oxidation by precipitating mag/haem

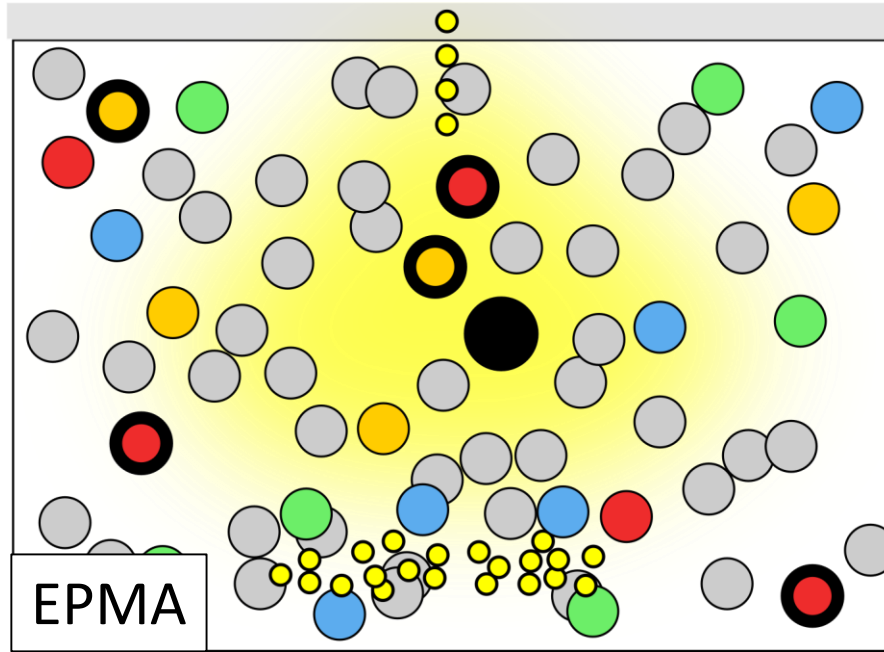
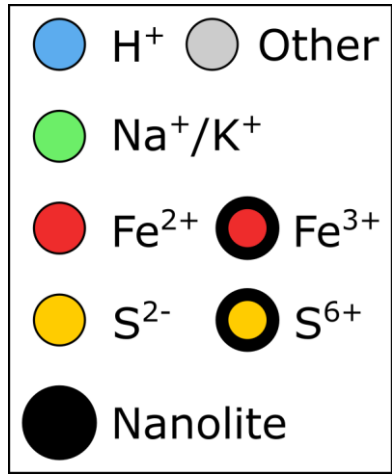
Hughes *et al.* (2018) *Am. Min.* 103:1445-1454

# Fe oxidation as $Fe^{2+}$ migrates faster than $Fe^{3+}$

Burgess *et al.* (2016) *Am. Min.* 101(12): 2677-2688

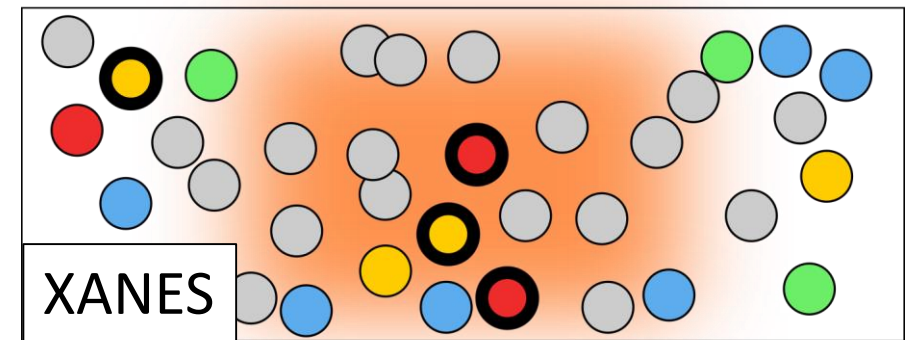
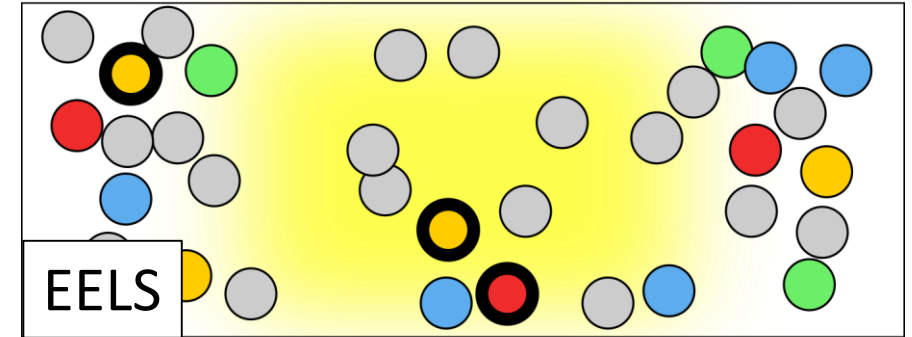


# Fe oxidation



If high Fe, oxidation by precipitating mag/haem  
Hughes *et al.* (2018) *Am. Min.* 103:1445-1454

Fe oxidation as  $Fe^{2+}$   
migrates faster than  $Fe^{3+}$   
Burgess *et al.* (2016) *Am. Min.* 101(12): 2677-2688



Oxidation for  $Fe^{2+}$  to  $Fe^{3+}$   
using O from  $H_2O$   
Cottrell *et al.* (2018) *Am. Min.* 103: 489-501

# Conclusions

- Fe (and S) redox changes are a common feature of electron (EPMA, EELS) and photon (XANES, Raman) beams
- Direction and rate of redox change depends on beam-type, glass composition, and analytical conditions
- More data needed to understand Fe redox changes in EELS and S redox changes in EPMA and XANES
- Lower dose helps to reduce damage BUT sacrifices spatial resolution