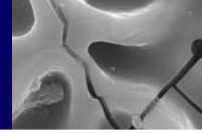


Water vapour corrosion of rare earth disilicates ($RE_2Si_2O_7$) in flowing hot atmospheres containing $Al(OH)_3$

Nicolas Maier, Klaus G. Nickel

- Eberhard-Karls-University, Applied Mineralogy, Tübingen, Germany -

&

Georg Rixecker

- Max-Planck-Institute for Metals Research, Stuttgart, Germany;
now with: Robert Bosch AG, Stuttgart, Germany -

Acknowledgments

My thanks to:

- My supervisors K. G. Nickel and G. Rixecker for their support

- At the Max-Planck-Institute in Stuttgart:
  → R. Mager for help with the corrosion testing equipment
  → U. Heinrichs, M. Schweizer & U. Schaefer for advice during sample preparation
  → The electron microscopy staff of the powder metallurgical laboratory for SEM pictures and EDX measurements

- At the University of Tübingen:
  → E. Nadler for SEM pictures

Outline

- Introduction
- Sample preparation and experimental setup
- Sample evolution during corrosion
- Theory for the observed phase development
- Mass losses
- Summary

Introduction

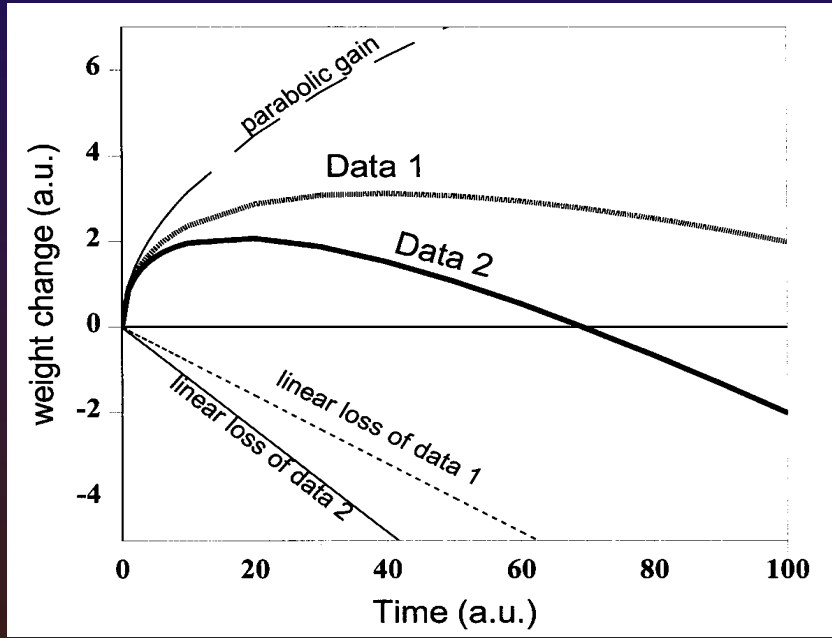
Why corrode rare earth disilicates?

$RE_2Si_2O_7$: candidates for EBC materials for the protection of Si-based ceramics (SiC, Si_3N_4) in hot wet environments

$SiC + 3H_2O(g) \rightarrow SiO_2 + 3H_2(g) + CO(g)$

$Si_3N_4 + 6H_2O(g) \rightarrow 3SiO_2 + 2N_2(g) + 6H_2(g)$

$SiO_2 + 2H_2O \rightarrow Si(OH)_4(g) \Uparrow$



From: Nickel et al (2000) in Riedel: Handbook of Ceramic Hard Materials, VCH Weinheim

Introduction

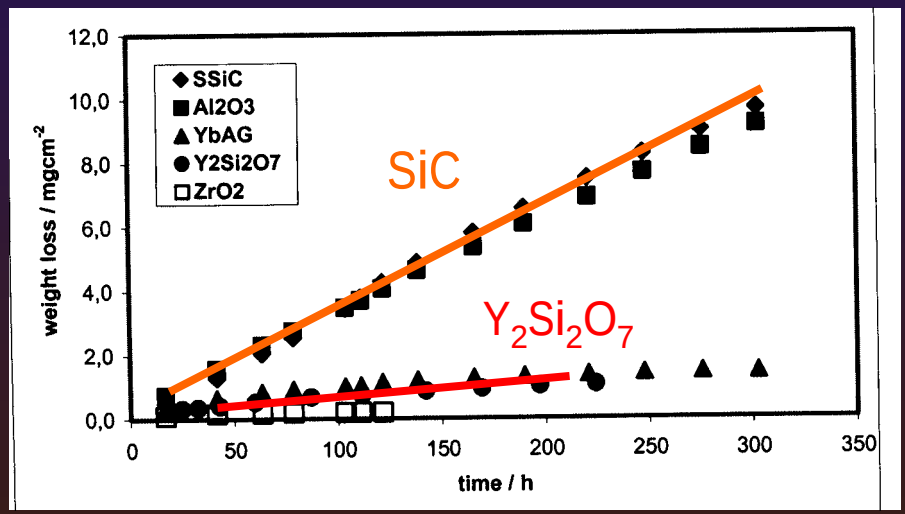
Rare earth disilicates

$$RE_2Si_2O_7 + 2H_2O \rightarrow RE_2SiO_5 + Si(OH)_4(g)$$

Low silica activities → less volatility / material loss than SiC, Si_3N_4

Low CTE mismatch

$RE_2Si_2O_7 \Leftrightarrow SiC$ / Si_3N_4

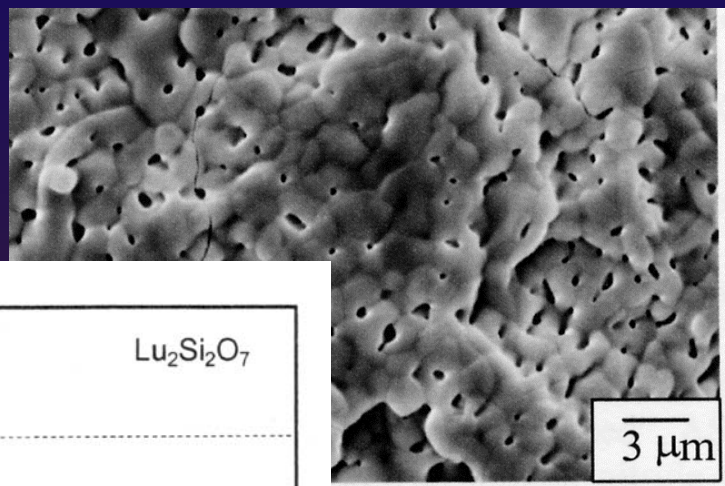


From: Klemm et al (in press) Proc. Cocoa Beach meeting 2004

Introduction

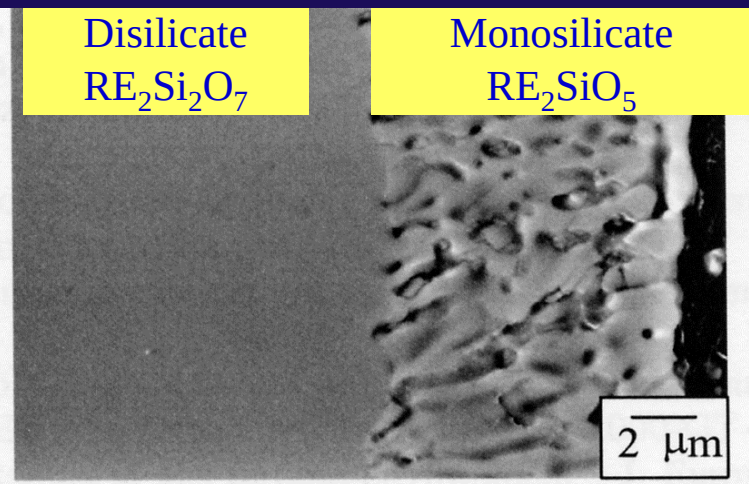
Expected corrosion behaviour

$$RE_2Si_2O_7 + 2H_2O \rightarrow RE_2SiO_5 + Si(OH)_4(g)$$

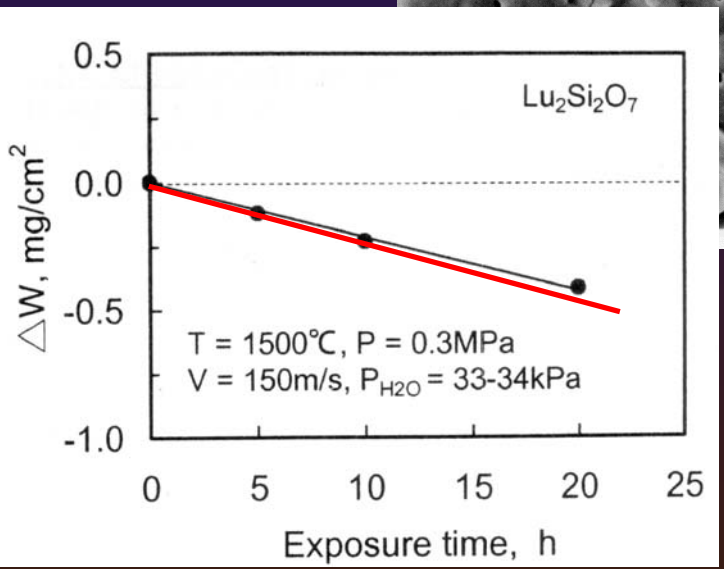


Disilicate $RE_2Si_2O_7$

Monosilicate RE_2SiO_5



From: Klemm et al (in press) Proc. Cocoa Beach meeting 2004



From: Yuri et al (2004) Proc. ASME Turbo Expo 2004

Introduction

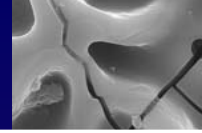
Intentions

* Up to now: only scarce and sometimes contadictory corrosion data for $RE_2Si_2O_7$

→ new data for a better understanding

* Better corrosion resistance of $RE_2Si_2O_7$ with small rare earth ions?

→ New findings concerning the hydro corrosion of $RE_2Si_2O_7$ in the presence of Al impurities



Sample preparation and experimental setup

Pressureless sintering of oxide powder mixtures

→ Disilicates of

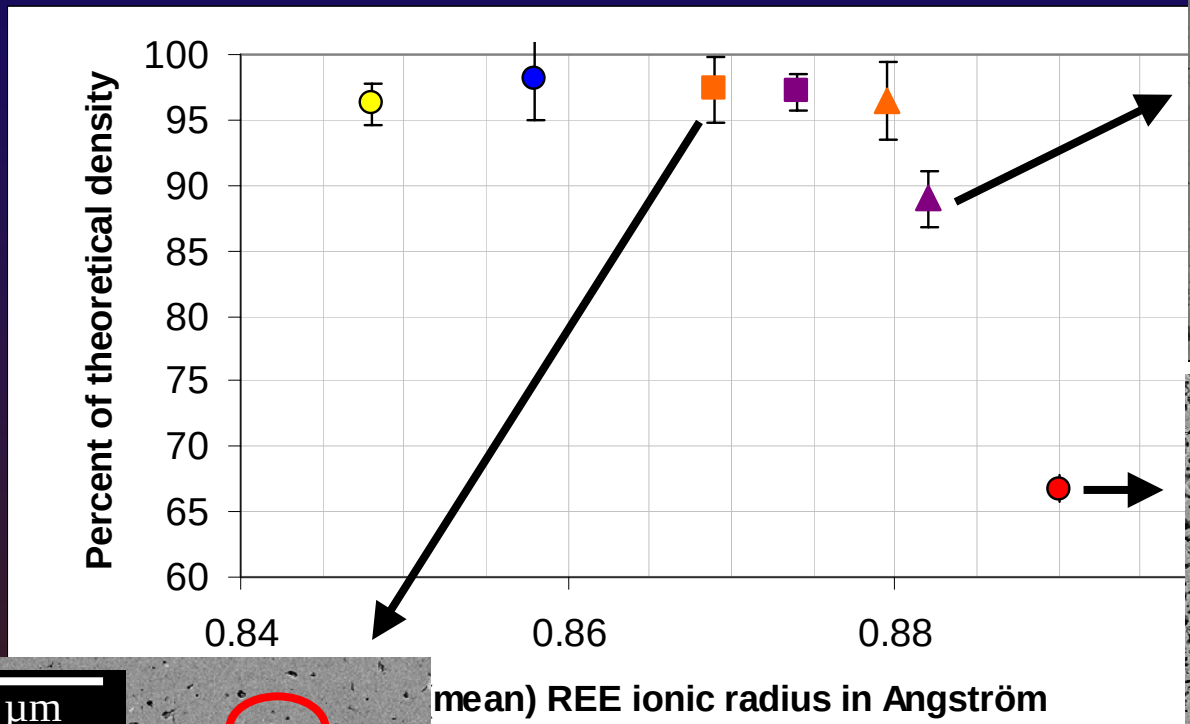
Lu **Yb** **Y**

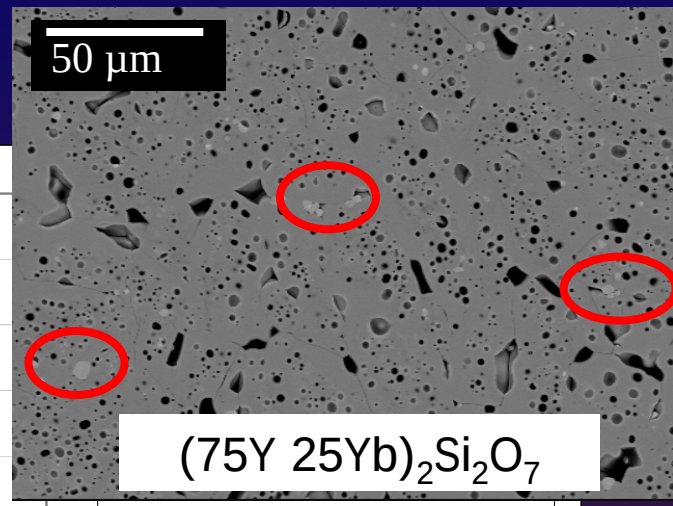
50 % Y 50 % Lu **50 % Y 50 % Yb**

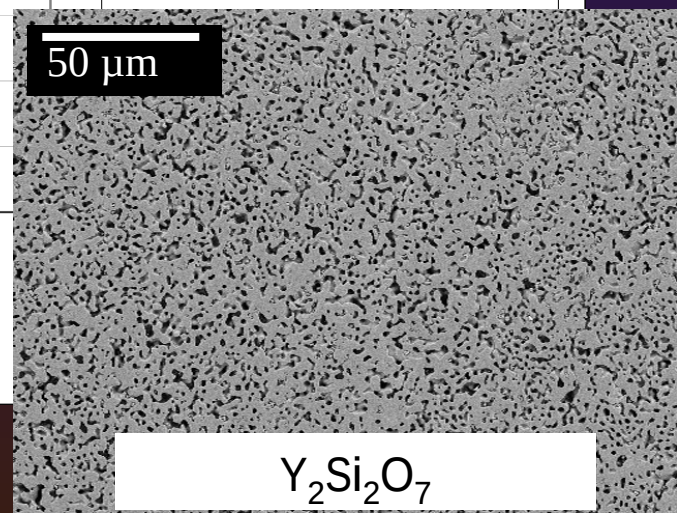
75 % Y 25 % Lu **75 % Y 25 % Yb**

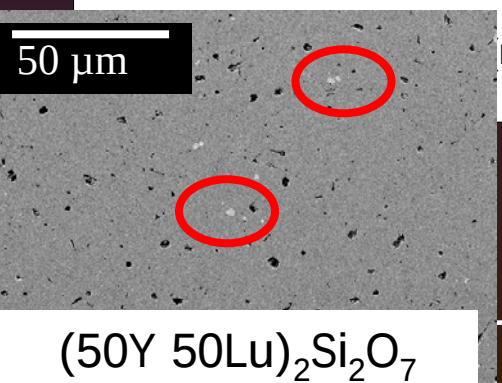
Sample preparation and experimental setup

Sintering densities





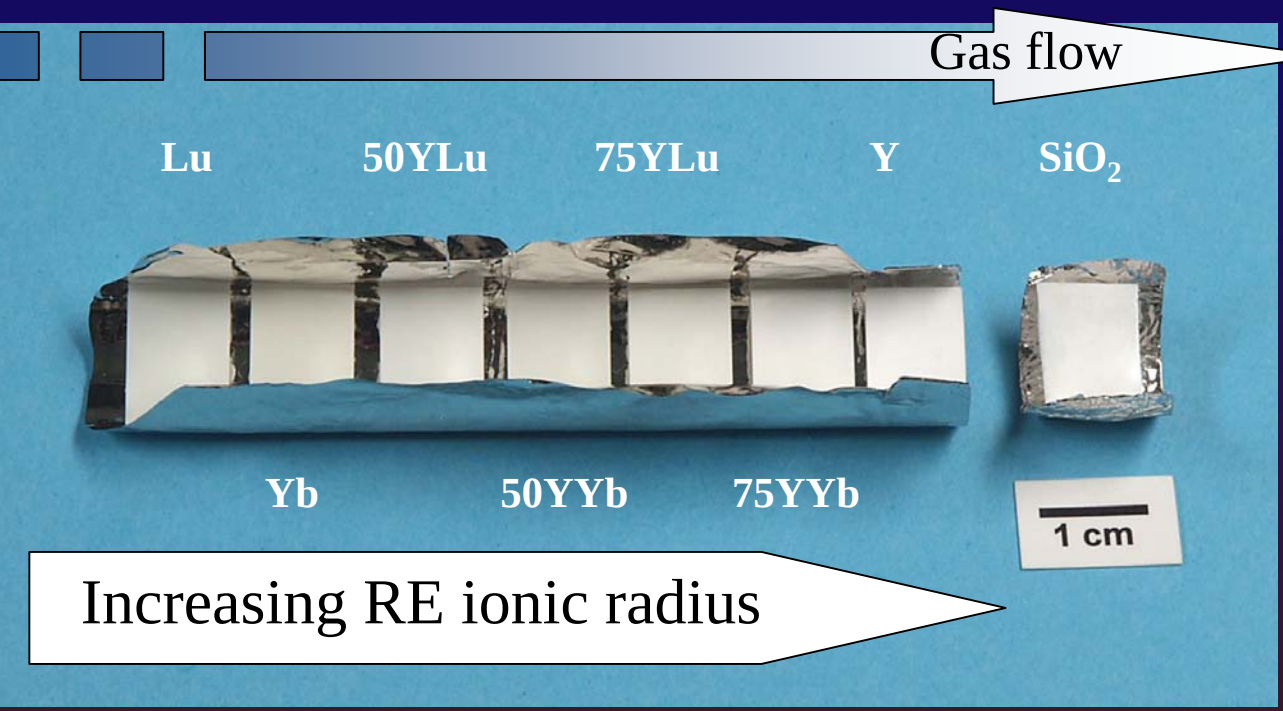


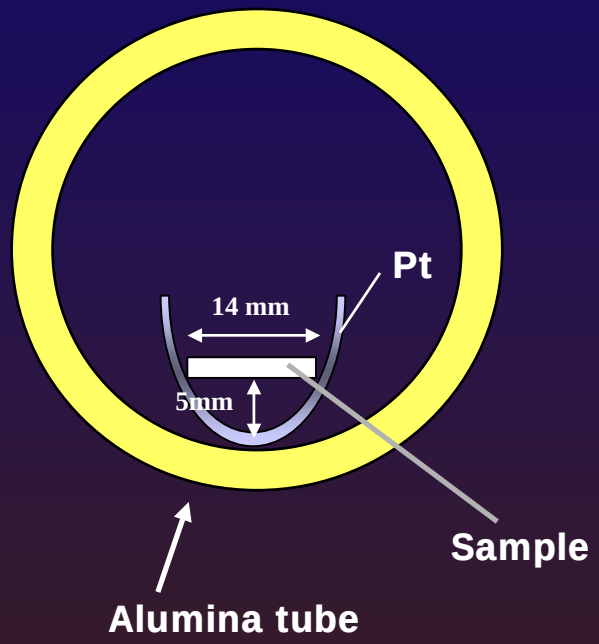


Monosilicate

RE_2SiO_5

Sample preparation and experimental setup

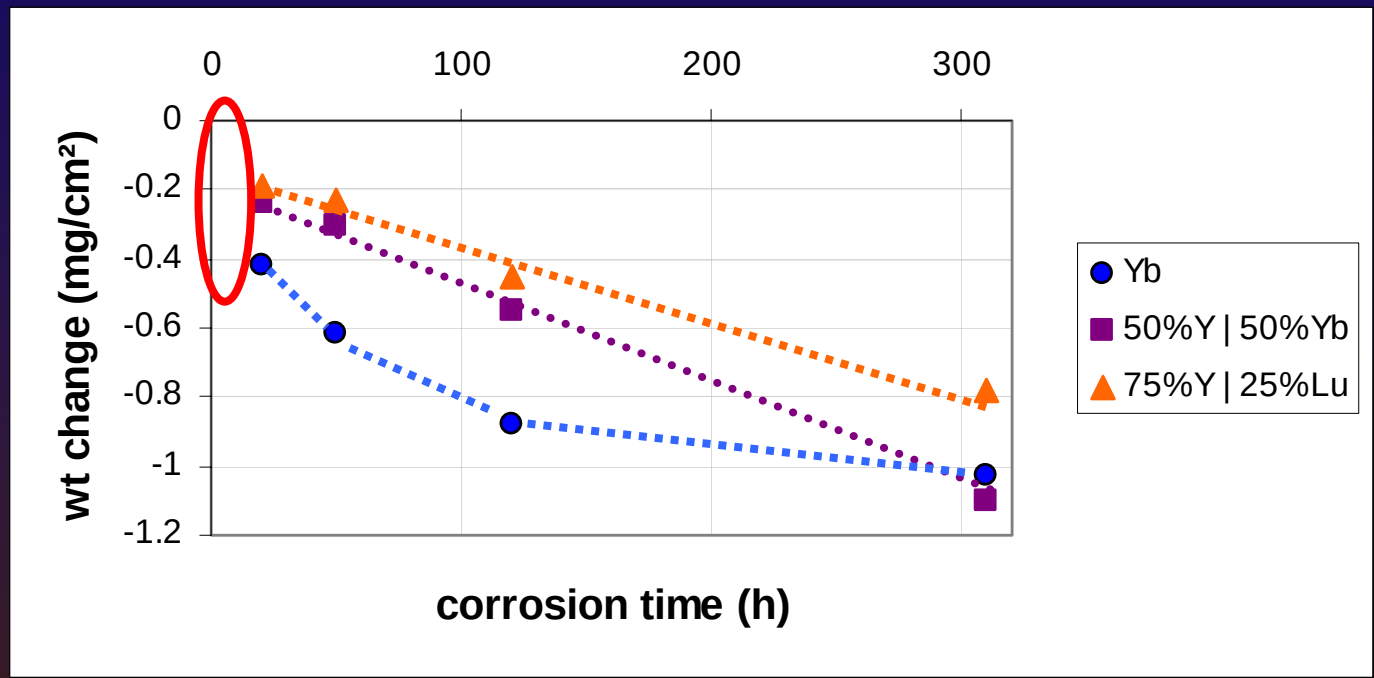




T = 1500°C, $\mathbf{v_{gas}}$ = 13 cm/s, $\mathbf{p_{total}}$ = 1 bar, $\mathbf{p_{H2O}}$ = 0,3 bar

Sample evolution during corrosion

Weight losses

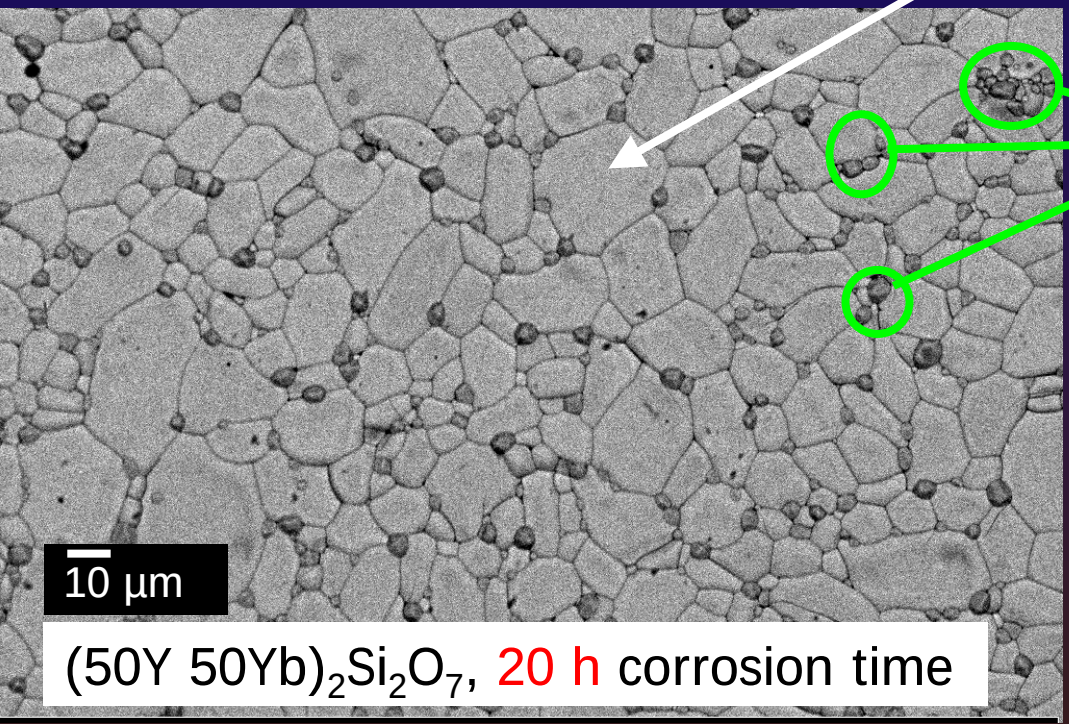


→ No simple linear kinetics as expected

→ Corrosion behaviour ≠ expectations

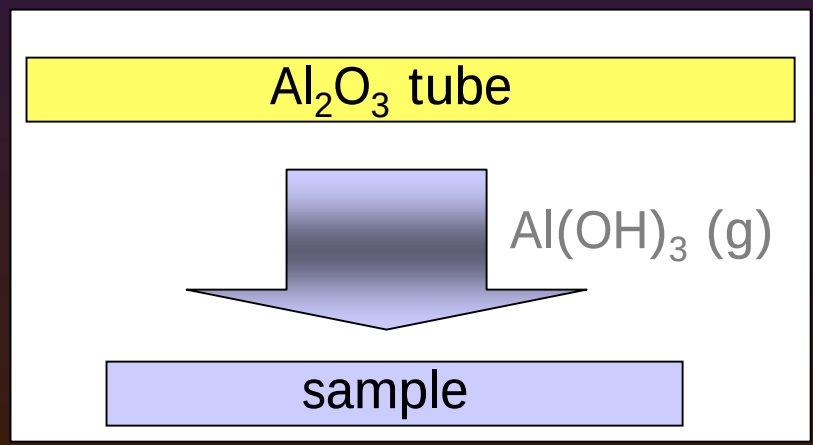
Sample evolution during corrosion

Evolution of the upper faces



$(50Y\ 50Yb)_2Si_2O_7$, 20 h corrosion time

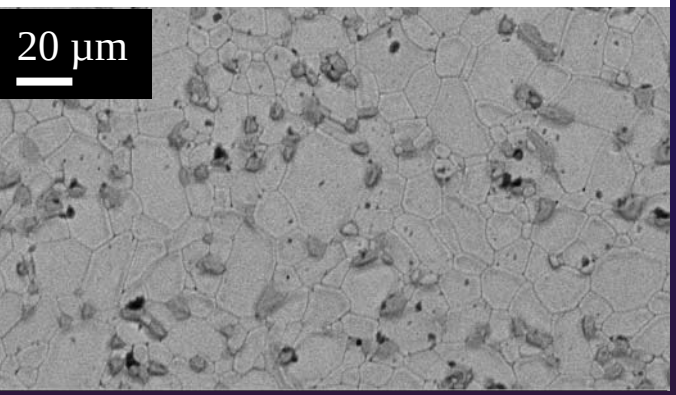
→ Al contamination!



Sample evolution during corrosion

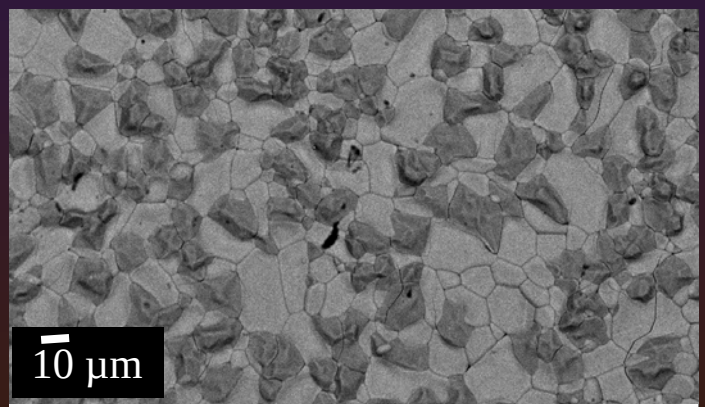
Evolution of the upper faces

$(50Y\ 50Yb)_2Si_2O_7$, 20 h corrosion time



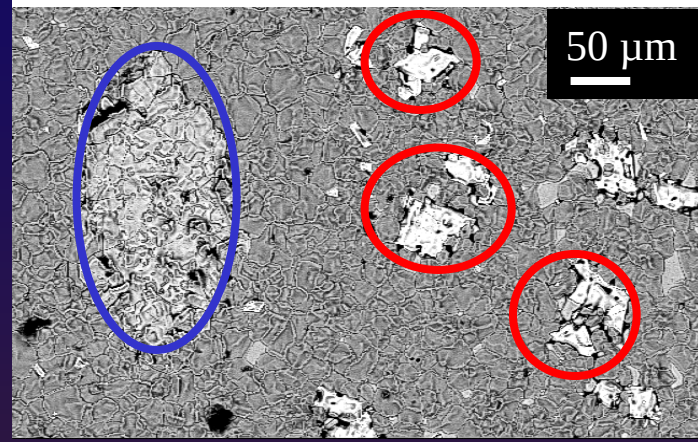
Monosilicate
RE_2SiO_5

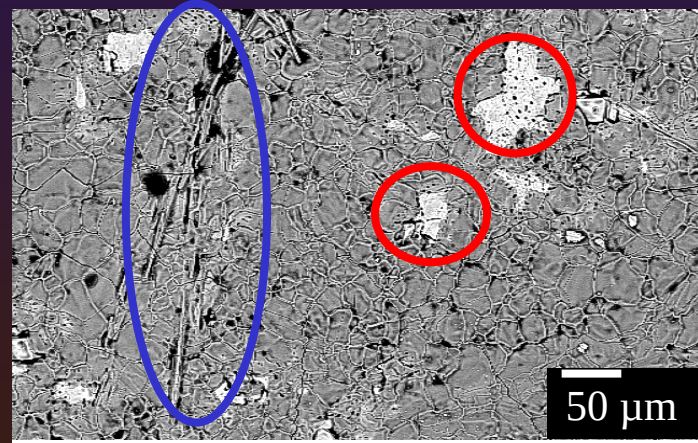
Apatite
$RE_{9.33}(SiO_4)_6O_2$
Ca-stabilised



$(50Y\ 50Yb)_2Si_2O_7$, 120 h corrosion time

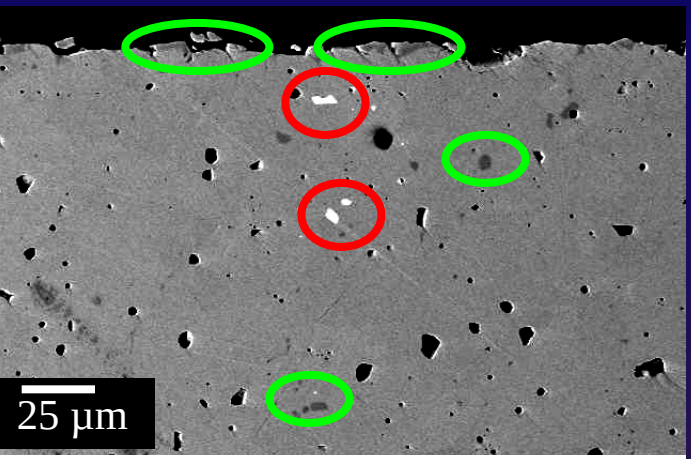
$(50Y\ 50Yb)_2Si_2O_7$, 310 h corrosion time





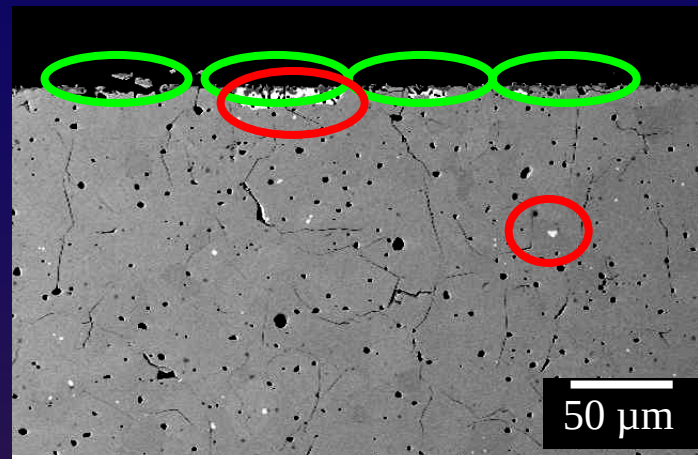
$(75Y\ 25Lu)_2Si_2O_7$, 310 h corrosion time

Water vapour corrosion of rare earth disilicates in hot atmospheres containing $Al(OH)_3$

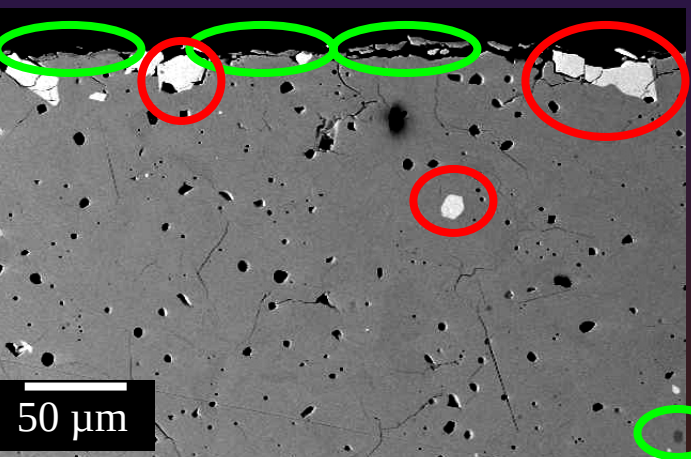


$(50Y\ 50Yb)_2Si_2O_7$, 120 h corrosion time

Garnet
$RE_3Al_5O_2$

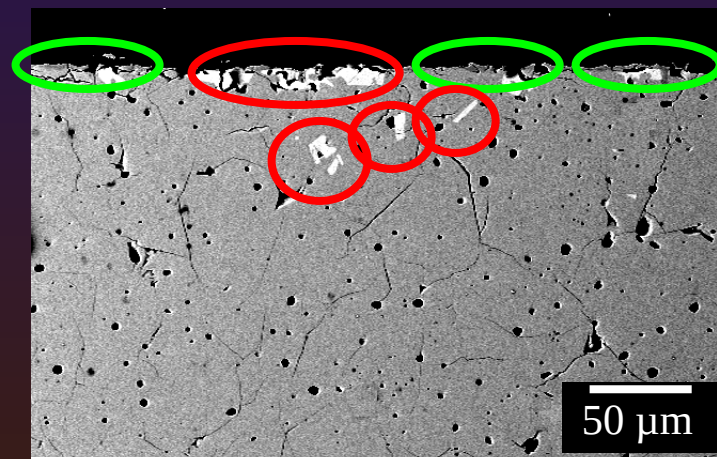


$Lu_2Si_2O_7$, 310 h corrosion time



$(50Y\ 50Yb)_2Si_2O_7$, 310 h corrosion time

Monosilicate
RE_2SiO_5
or
Apatite
$RE_{9.33}(SiO_4)_6O_2$
[with Ca]

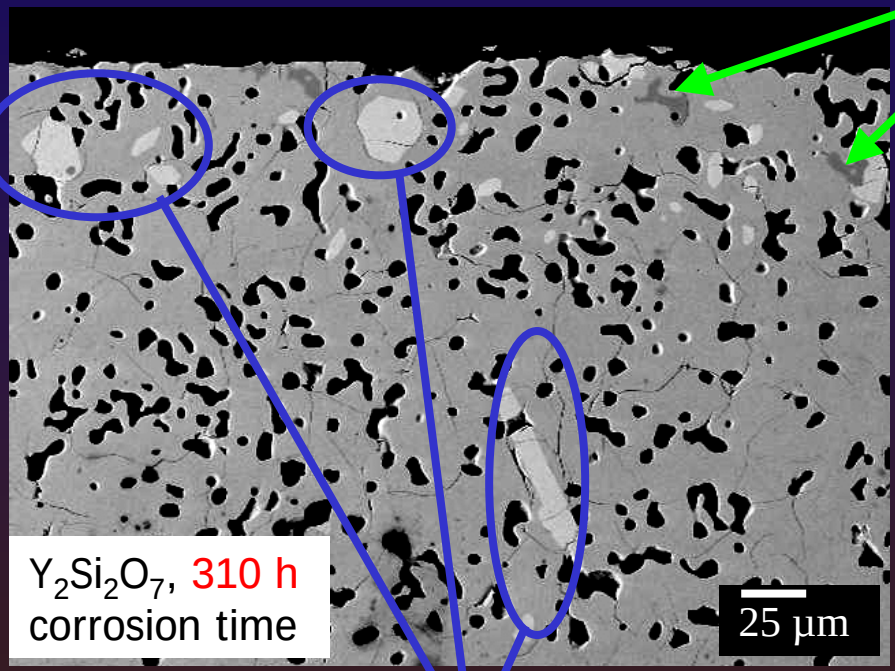


$(50Y\ 50Lu)_2Si_2O_7$, 310 h corrosion time

Sample evolution during corrosion

Evolution of the upper faces

Garnet $RE_3Al_5O_{12}$



Apatite $RE_{9.33}(SiO_4)_6O_2$ with Ca

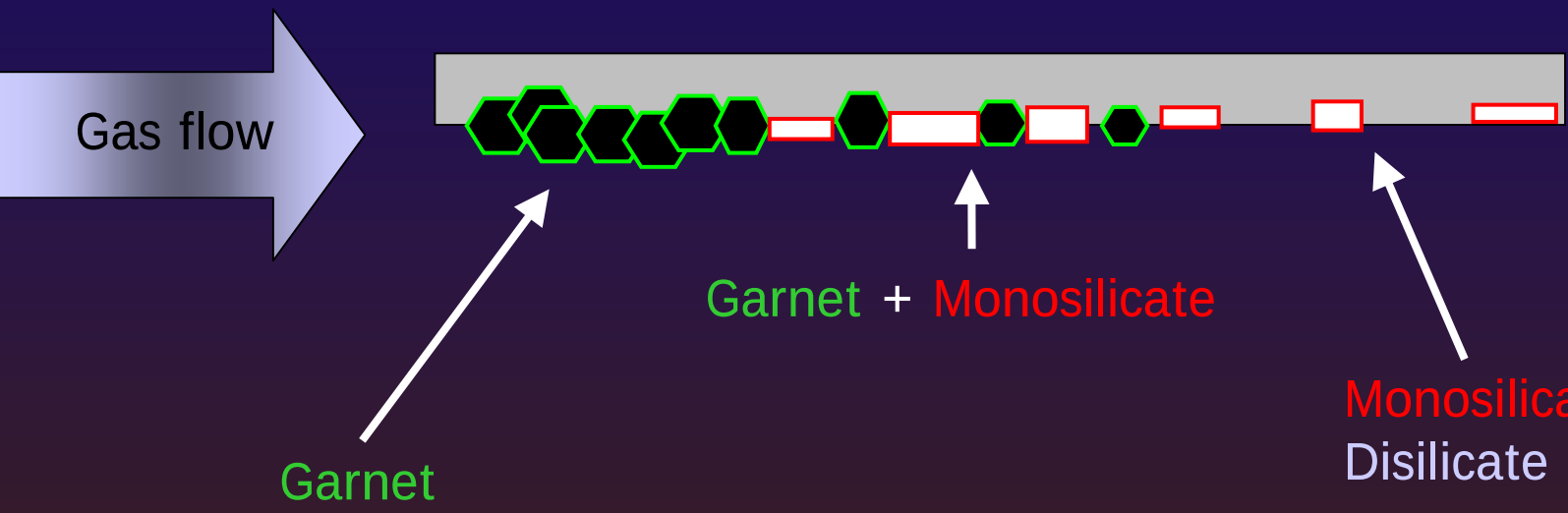
Highly porous $Y_2Si_2O_7$:

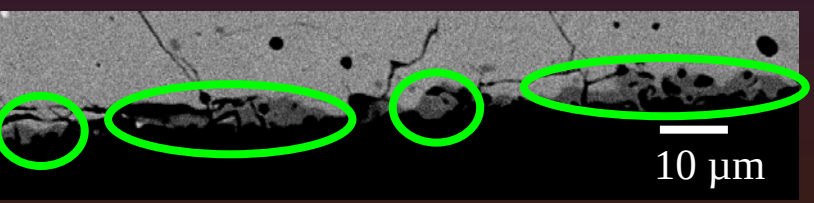
Strong corrosive alteration reaches deep into the bulk

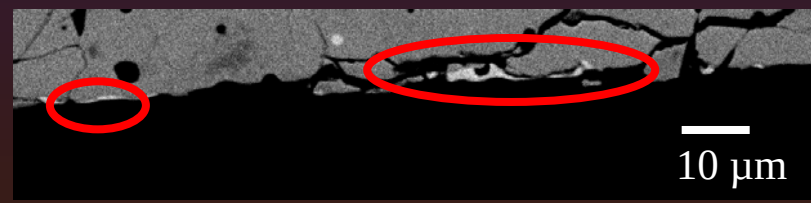
Sample evolution during corrosion

Evolution of the lower faces

First sample in the sequence: $Lu_2Si_2O_7$



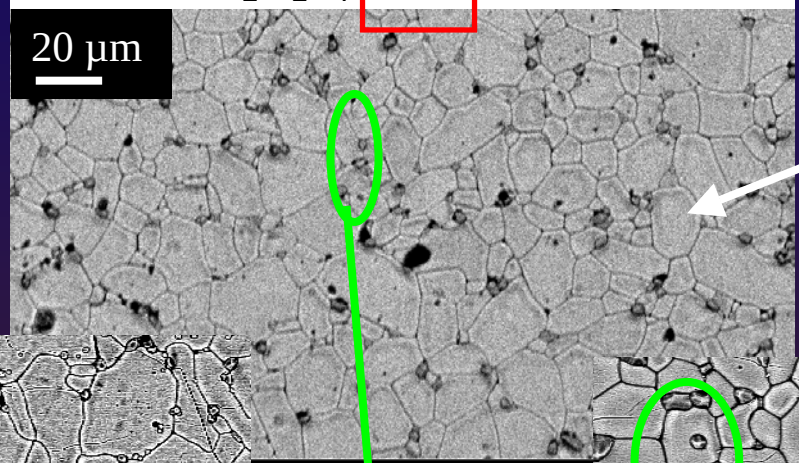




Sample evolution during corrosion

Evolution of the lower faces

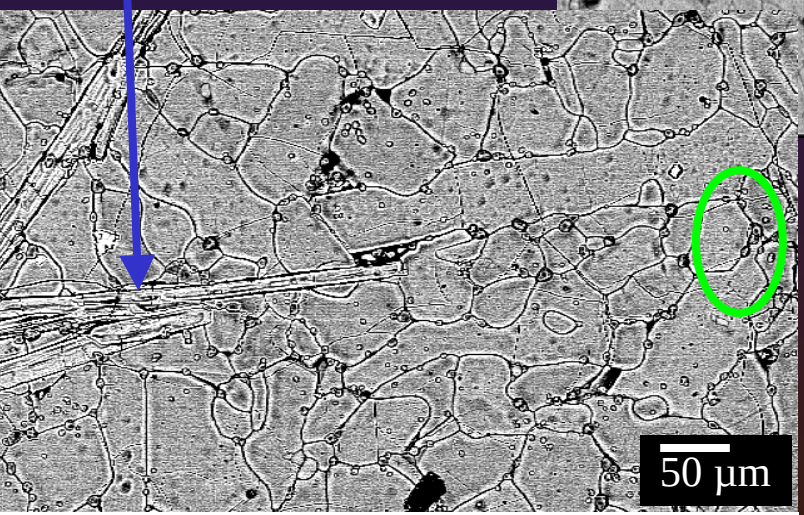
$(50Y\ 50Yb)_2Si_2O_7$, 20 h corrosion time



Apatite
$RE_{9.33}(SiO_4)_6O_2$
with Ca

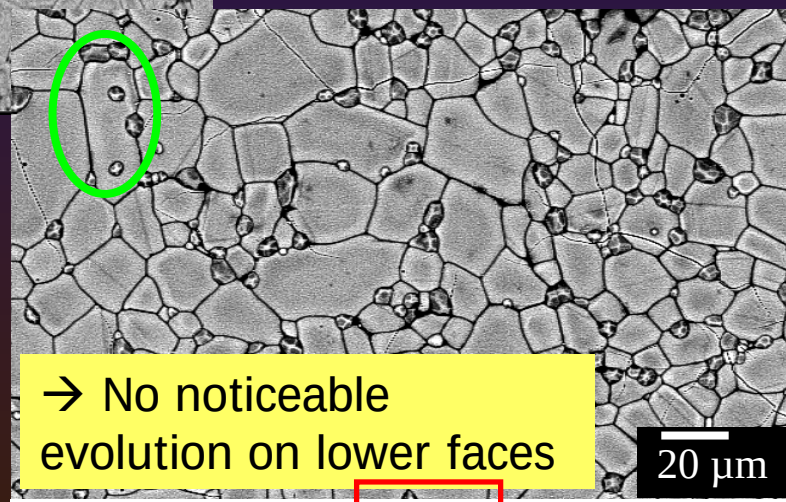
Disilicate
$RE_2Si_2O_7$

Garnet
$RE_3Al_5O_{12}$



$(75Y\ 25Lu)_2Si_2O_7$, 310 h corrosion time

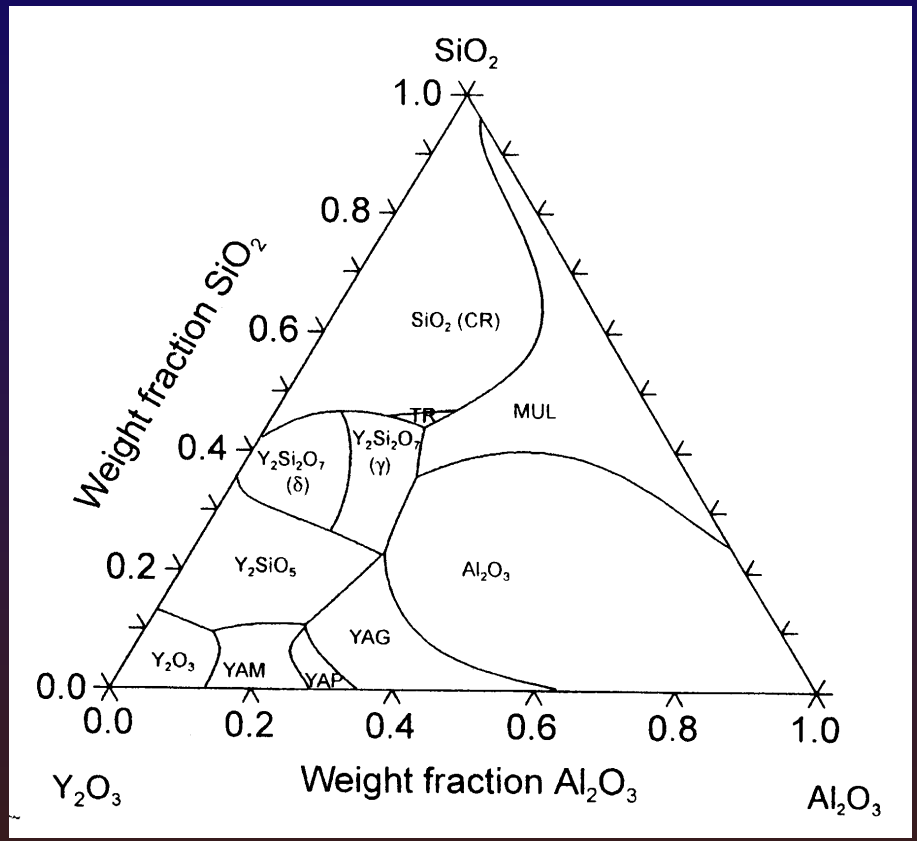
Other samples



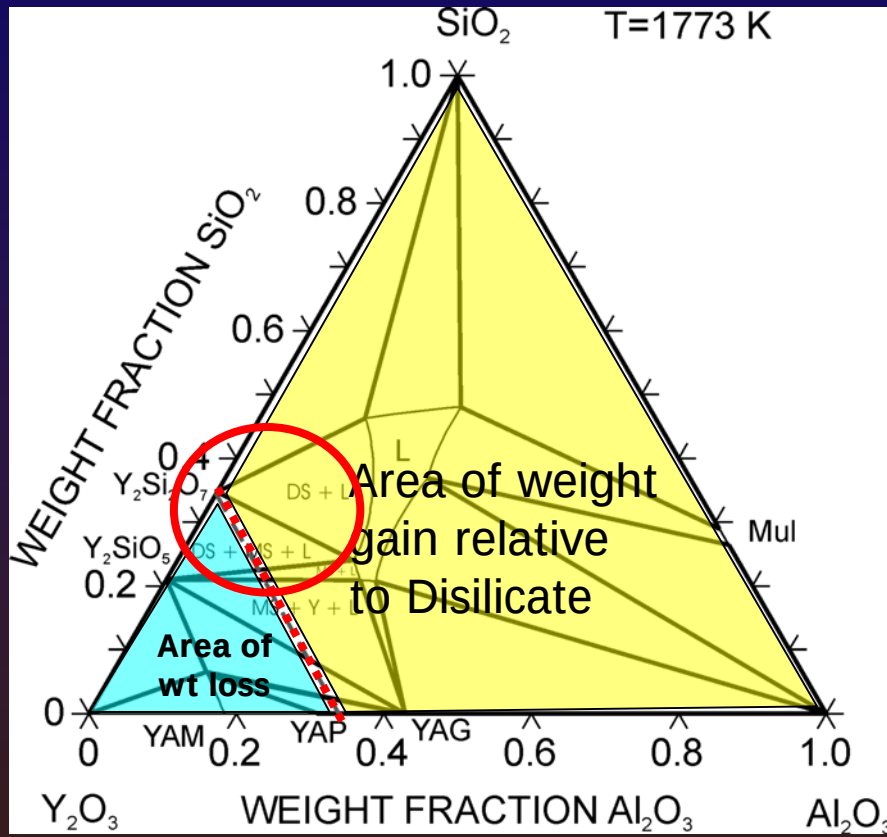
→ No noticeable evolution on lower faces

$(50Y\ 50Yb)_2Si_2O_7$, 310 h corrosion time

Theory for the observed phase development



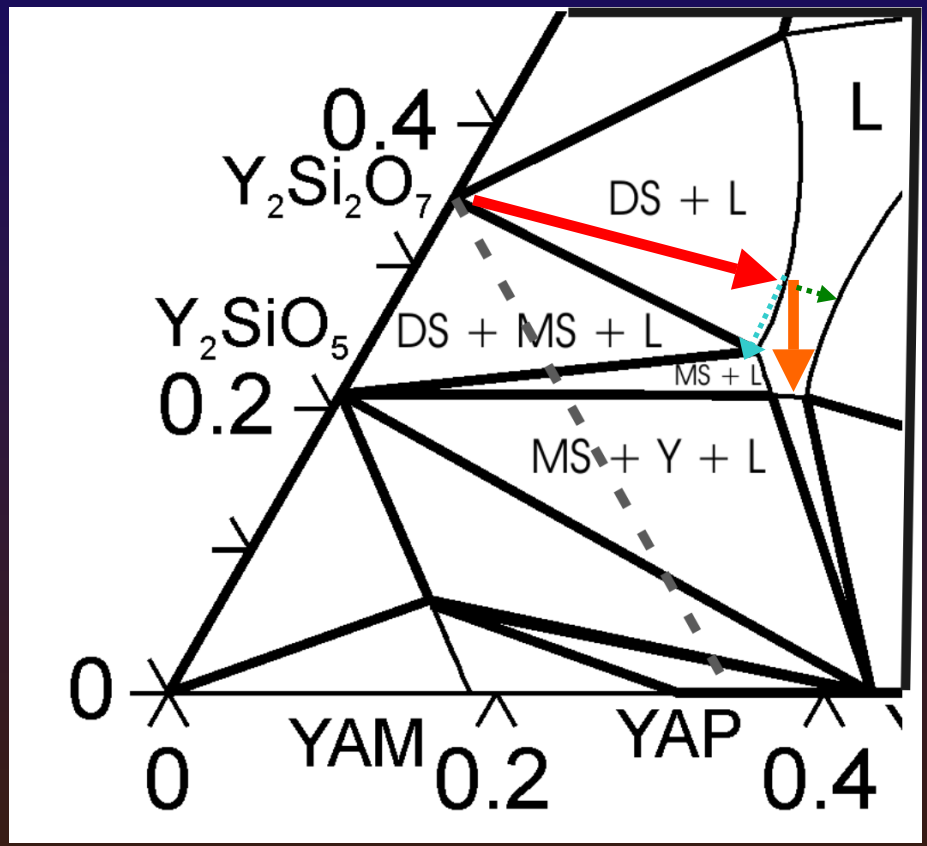
From: Fabrichnaya et al (2001): Z.Metallkd. 92

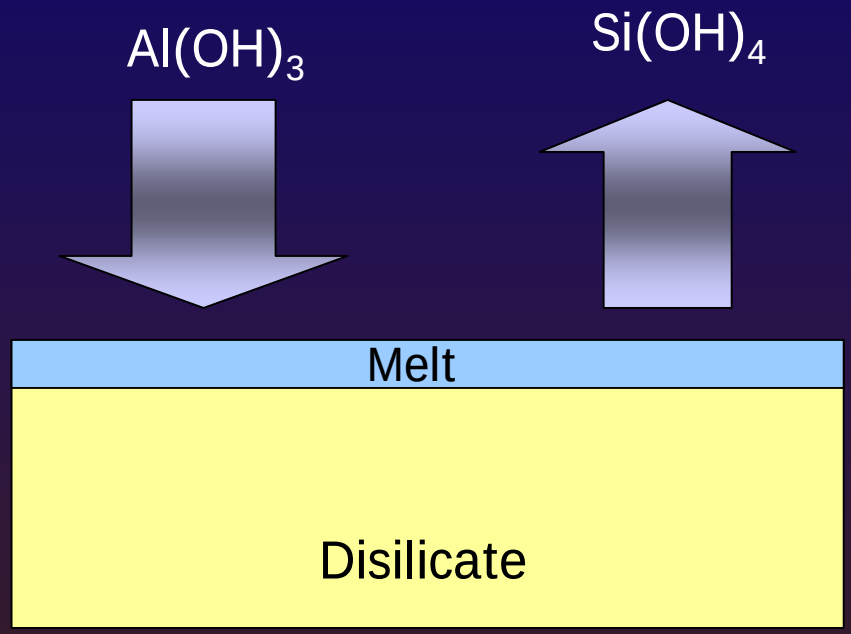


Calculated by O. Fabrichnaya on the basis of data from Fabrichnaya et al (2001): Z. Metallkd. 92

Theory for the observed phase development

Evolution of the upper faces



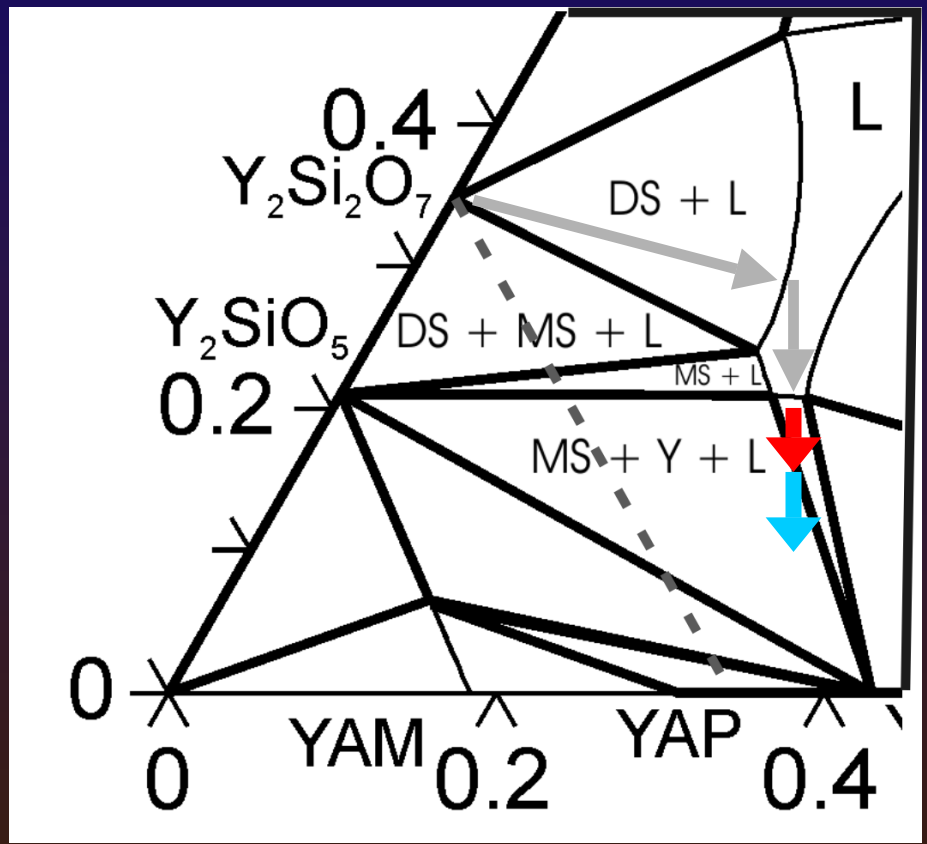


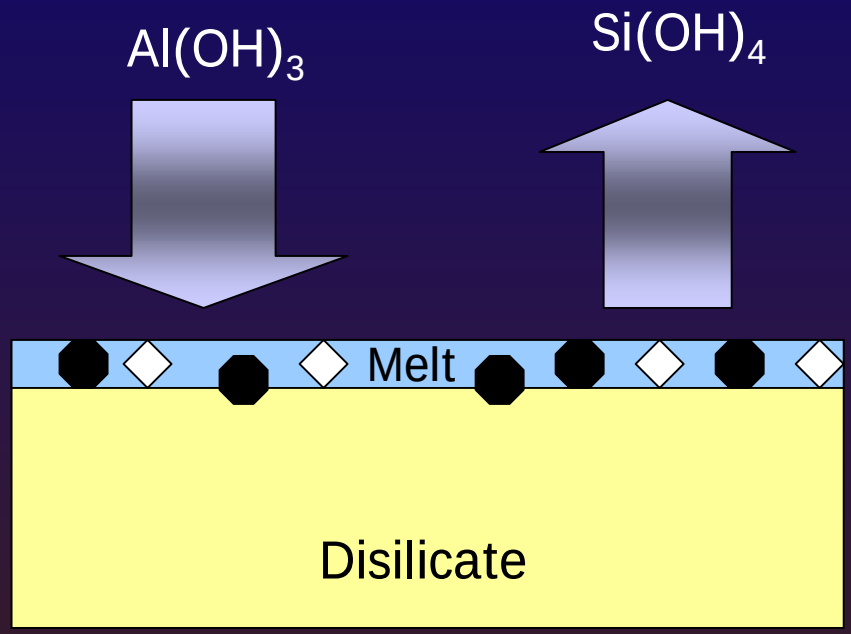
* Melt formation on Al uptake

* Si loss from the melt

Theory for the observed phase development

Evolution of the upper faces

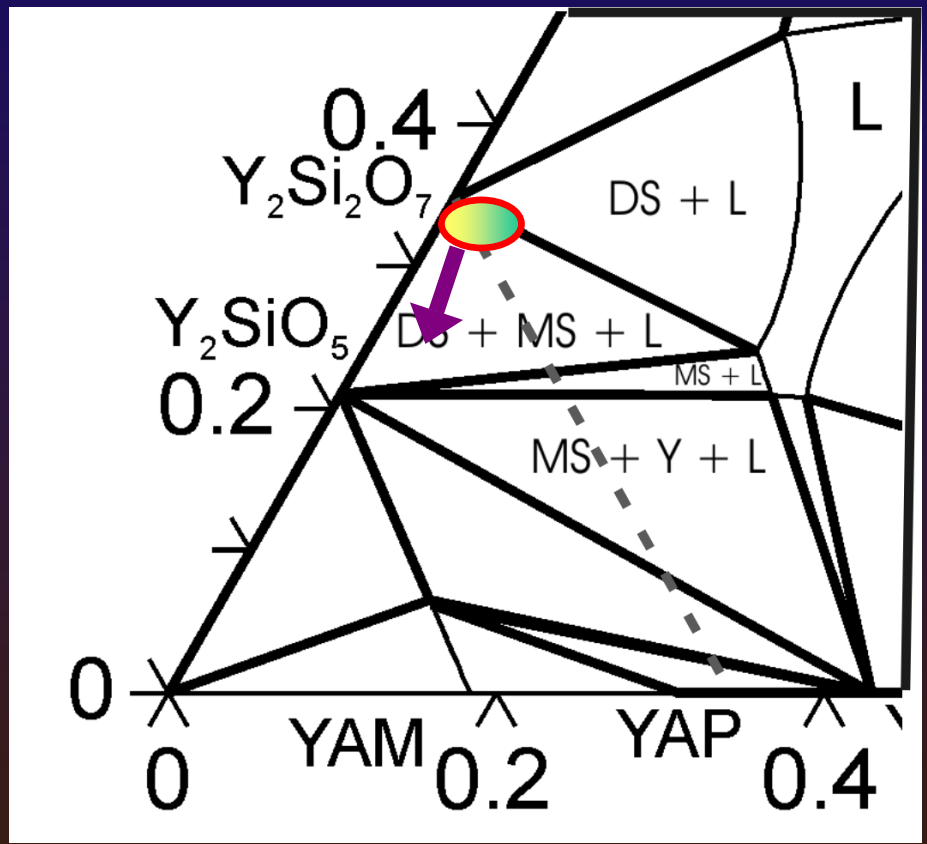


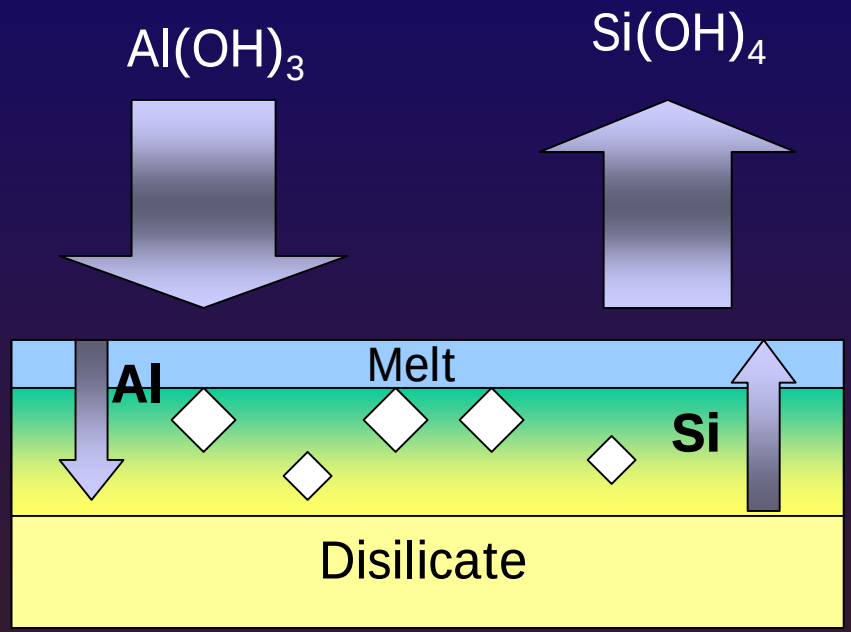


* Further Silica loss: formation of Garnet
* In later stages: formation of Monosilicate / Apatite possible

Theory for the observed phase development

Evolution of the upper faces

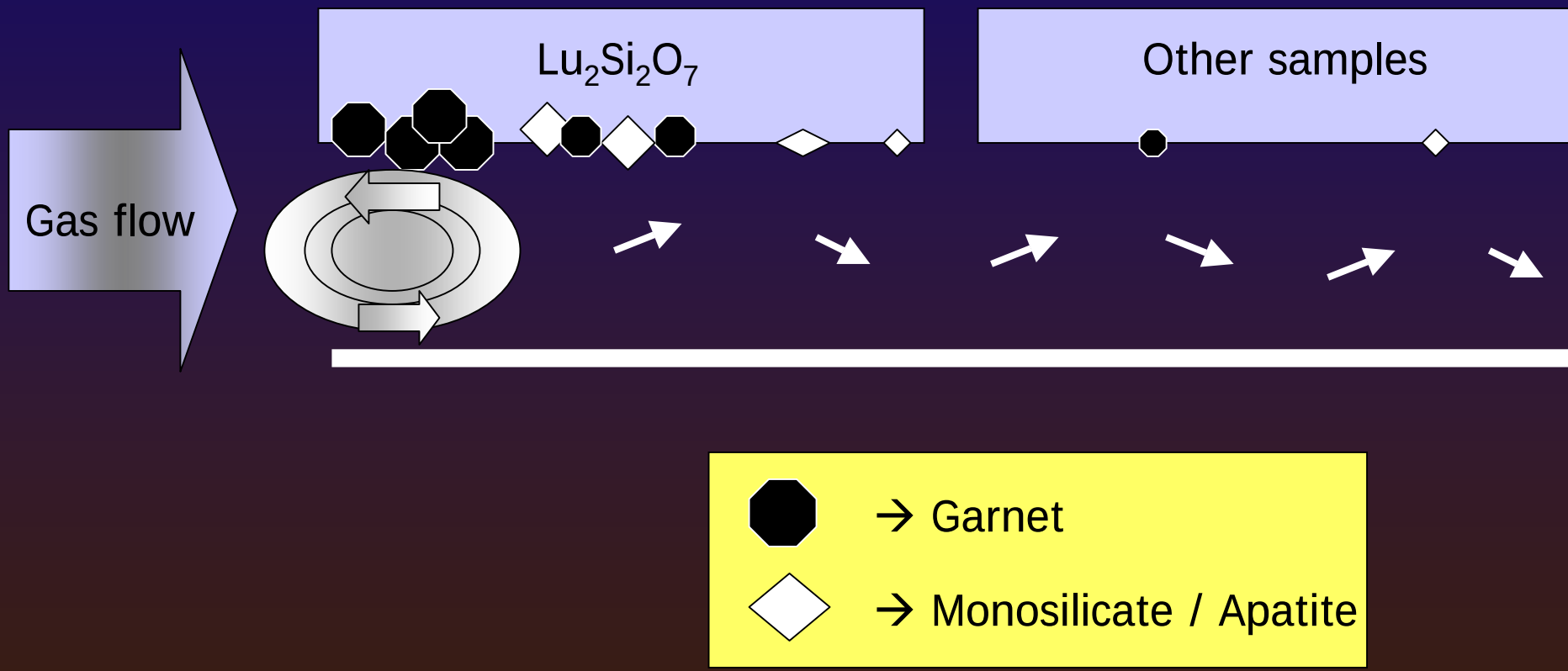




* Formation of a subsurface layer (with low contents of Al and Si) by diffusion of elements

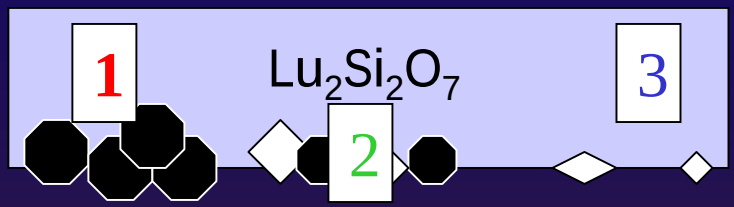
Theory for the observed phase development

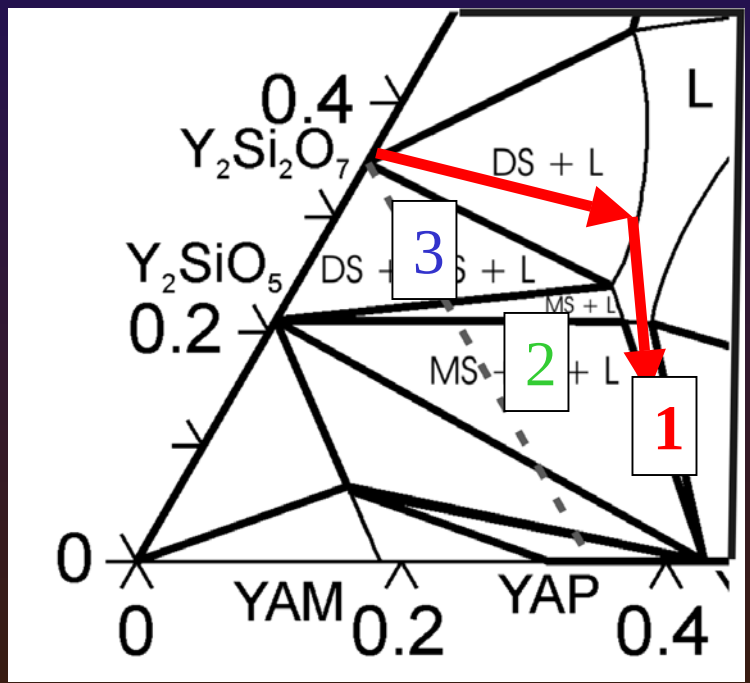
Evolution of the lower faces



Theory for the observed phase development

Evolution of the lower faces

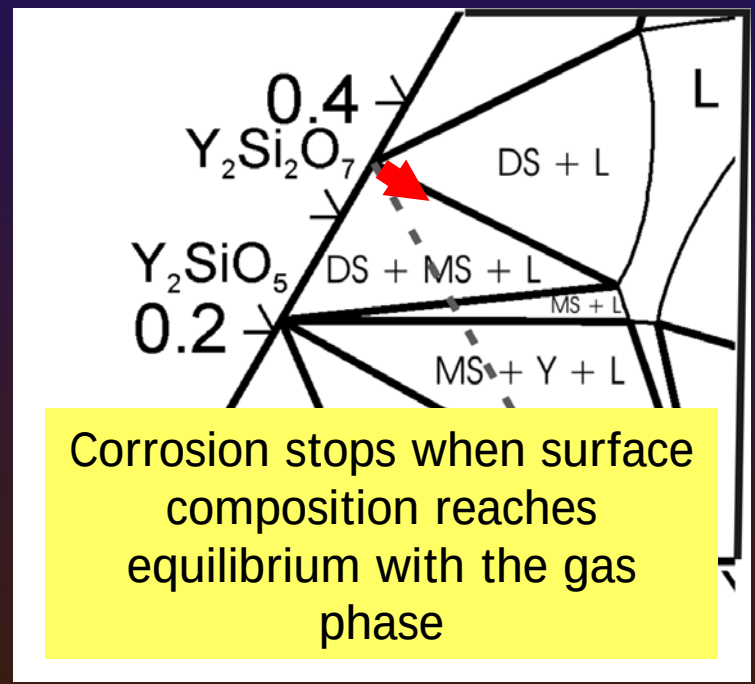




Other samples

Al

Si



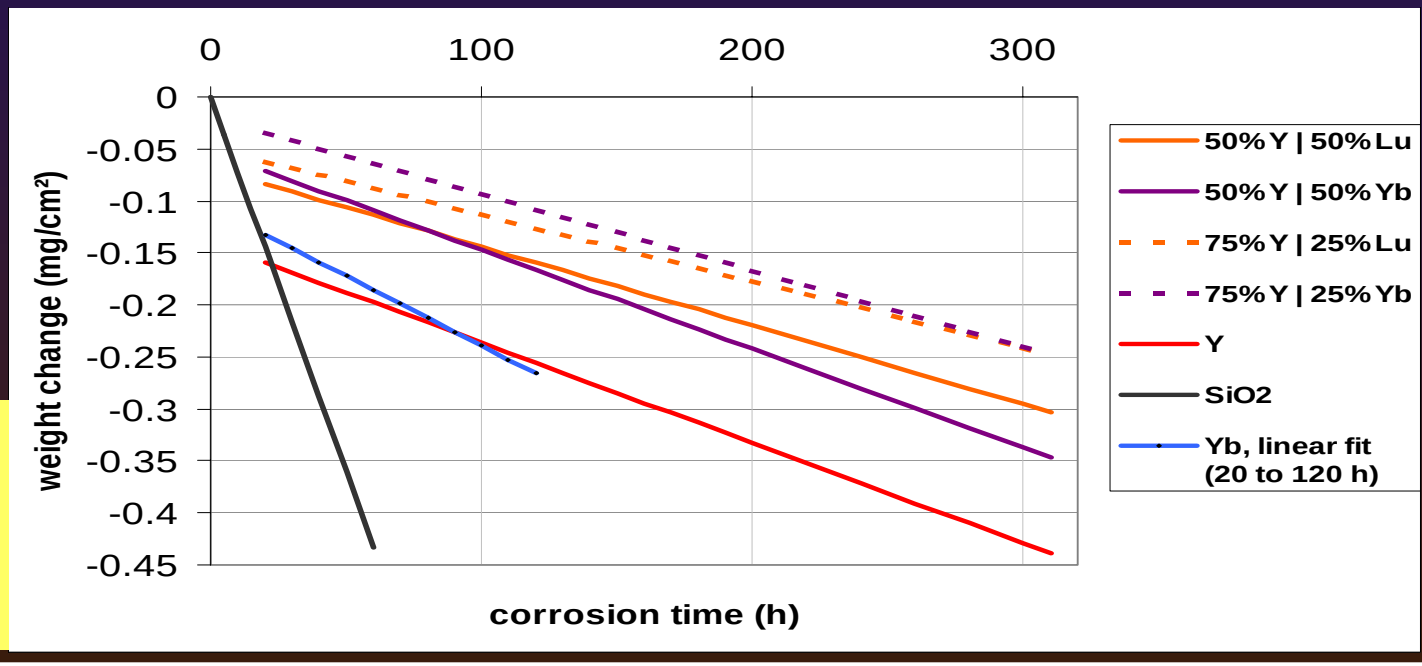
Corrosion stops when surface composition reaches equilibrium with the gas phase

Mass losses

General behaviour of the weight loss curves in accordance with corrosion model:

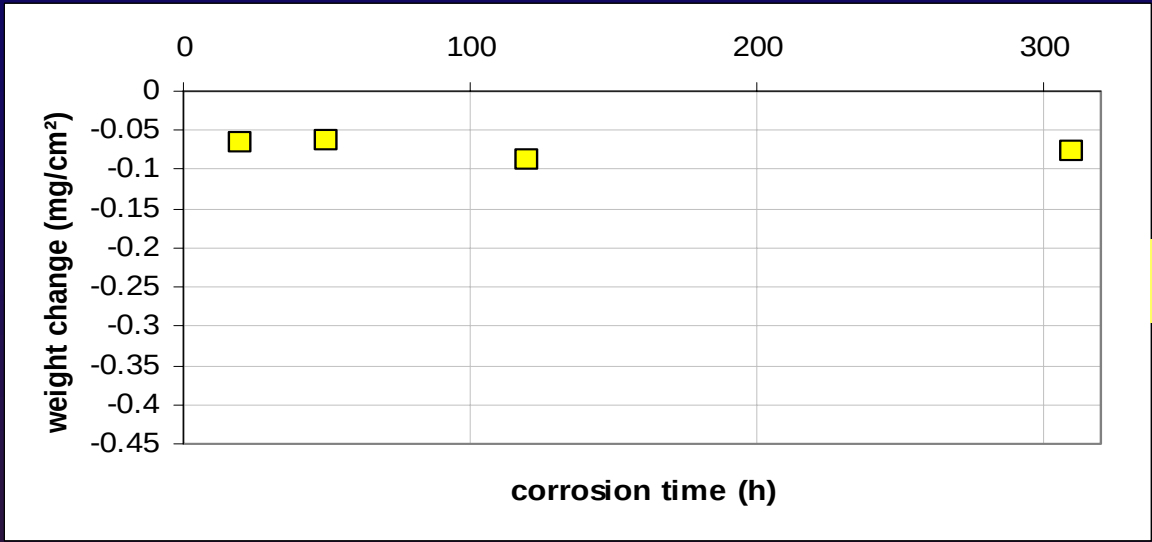
* High losses in an initial stage when a silica-rich melt interacts with the gas phase

* Slower (linear) rates in later stages when a melt with a fixed, lower silica activity interacts with the atmosphere



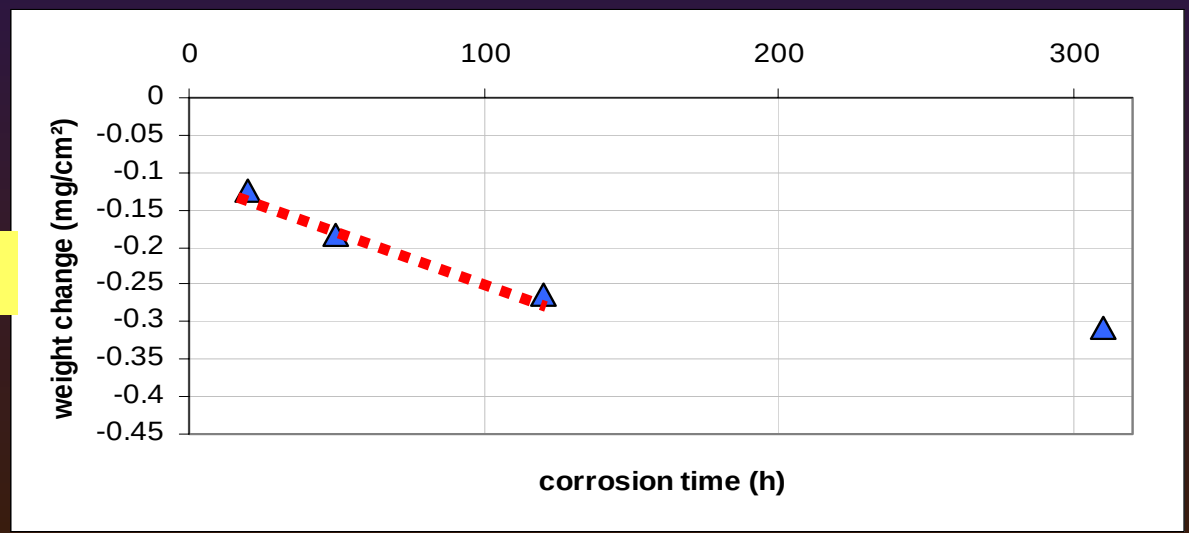
Linear fits of weight changes for t > 20 h

Mass losses

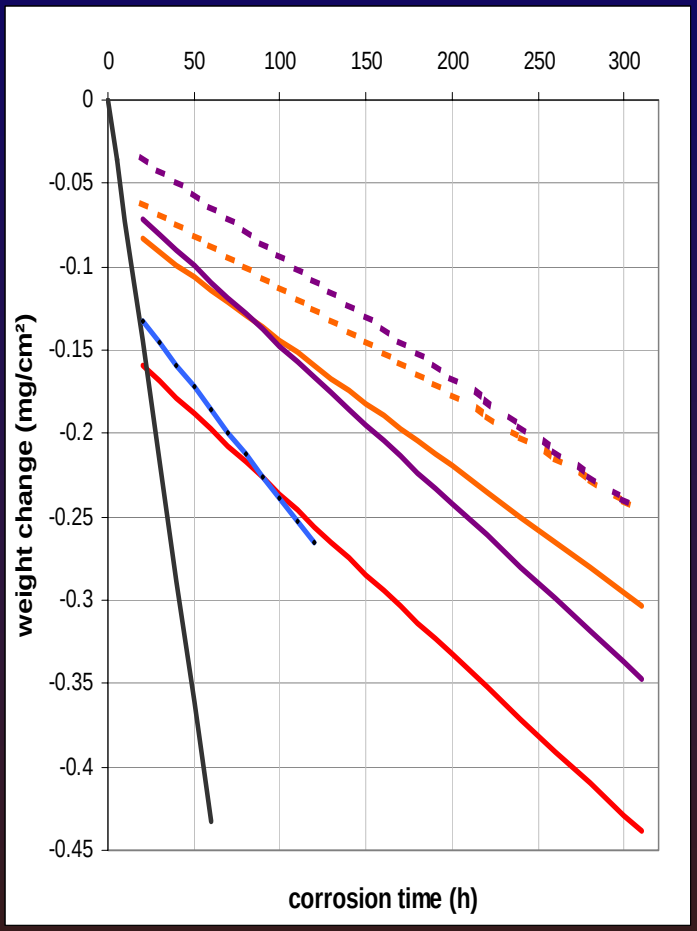


$Lu_2Si_2O_7$

$Yb_2Si_2O_7$



Mass losses



Weight loss rates (*10^{-3} mg/cm²h)

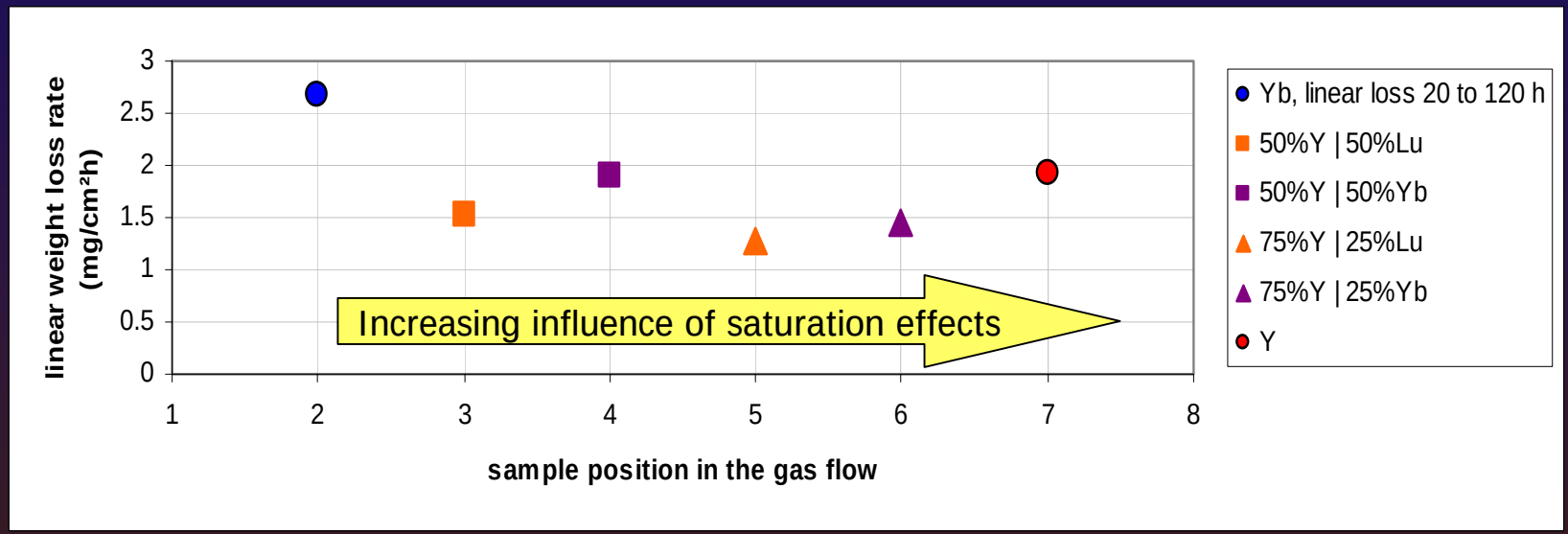
Yb	50%Y 50%Lu	50%Y 50%Yb	75%Y 25%Lu	75%Y 25%Yb	Y	SiO_2
1.34	**0.76**	**0.95**	**0.64**	**0.73**	**0.96**	**7.21**
⇓	⇓	⇓	⇓	⇓	⇓	
2.68	**1.52**	**1.90**	**1.28**	**1.46**	**1.92**	

Gas flow direction

Mass losses

Only limited significance of the measured weight loss rates

1) Saturation effects show clear influence on corrosion / weight loss rates



2) Al uptake: corrosive alteration connected with <u>weight gain</u>

→ as long as Al uptake cannot be quantified: measured weight loss gives no information about extent of material damage

Mass losses

Comparison with literature data

Literature data:

T, v_{gas}, p_{H2O}, p_{total}

Gas diffusion model

→ → → → → →

(E. J. Opila and others)

$T = 1500°C$

$V_{gas} = 13$ cm/s

$p_{H2O} = 0{,}3$ bar

$P_{total} = 1$ bar

$$K_l \propto (v_{gas}^{1/2} * p_{H2O}^{2}) / p_{total}^{1/2}$$

$$K_l \propto \exp (E_a / RT)$$

(simplified expressions)

Mass losses

Weight loss rates (*10^{-3} mg/cm²h):

	Our experiments	Lee et al[1] (converted)	Klemm et al[2] (converted)	Yuri et al[3] (converted)
$Yb_2Si_2O_7$	≈ 2.6	≈ 1.5	≈ 0.1 (1450°C)	
$Lu_2Si_2O_7$				≈ 1 *(porous sample with some free SiO_2)*
$Y_2Si_2O_7$	≈ 1.9		≈ 0.1 (1450°C)	

Al contamination

1 = J. Eur. Cer. Soc. 25, 2005

2 = Proc. Cocoa Beach Meeting 2005, in press

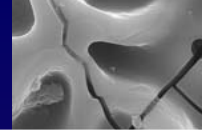
3 = Proc. ASME Turbo Expo 2004

Mass losses

Higher corrosion rates in atmospheres containing $Al(OH)_3$

1) Intensifying effect of $Al(OH)_3$ on the silica loss from the samples?

2) $Si(OH)_4$ saturation of the gas phase when SiC or SiO_2 furnace tubes are used?



Summary

* Hydro corrosion behaviour of $RE_2Si_2O_7$ with Al contamination different from the behaviour without it

→ Corrosion by the formation of a melt which loses Si to the atmosphere

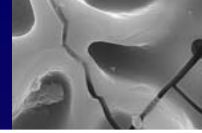
→ Layered structure: garnet at the surface, silica depleted phases without Al below

→ Corrosive alteration reaches deep into the material

→ Formation of new phases can cause cracking

→ Fast weight loss rates in an early stage of corrosion, slower rates after some hours

→ Weight loss rates > weight loss rates measured without Al contamination in SiC tubes (despite saturation and Al incorporation effects)



Thank you for your attention!