“The influence of melt composition on the local structure around trace elements in glasses and melts with implications for crystal-melt partitioning”

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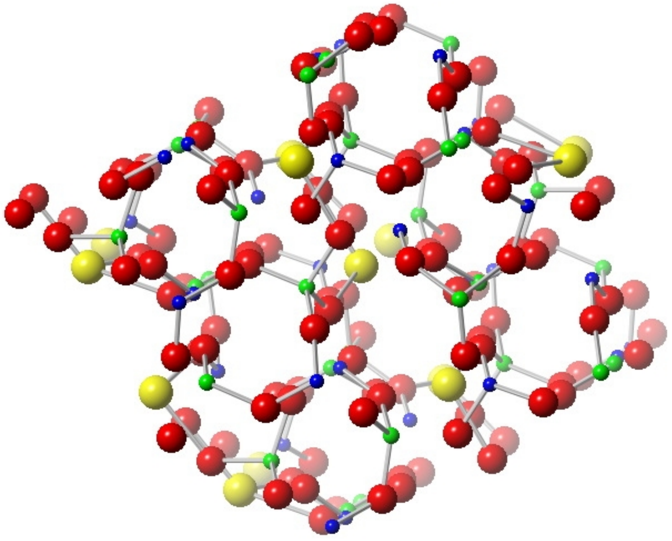
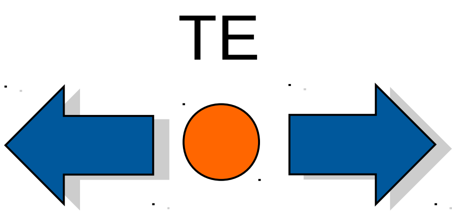
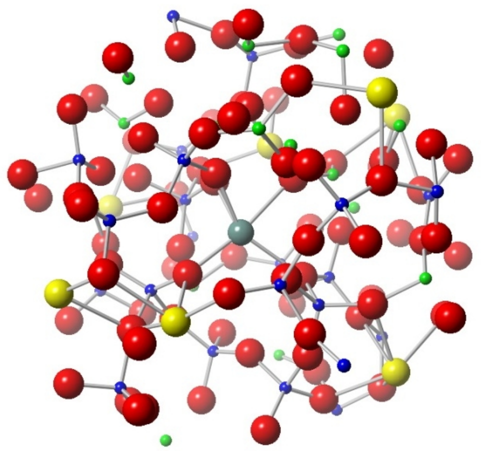
Introduction

"Trace elements (TE) are important indicators in magmatic and metamorphic rocks on Earth, Moon and the terrestrial planets."

Partitioning is a thermodynamic process => minimization of the free energy.







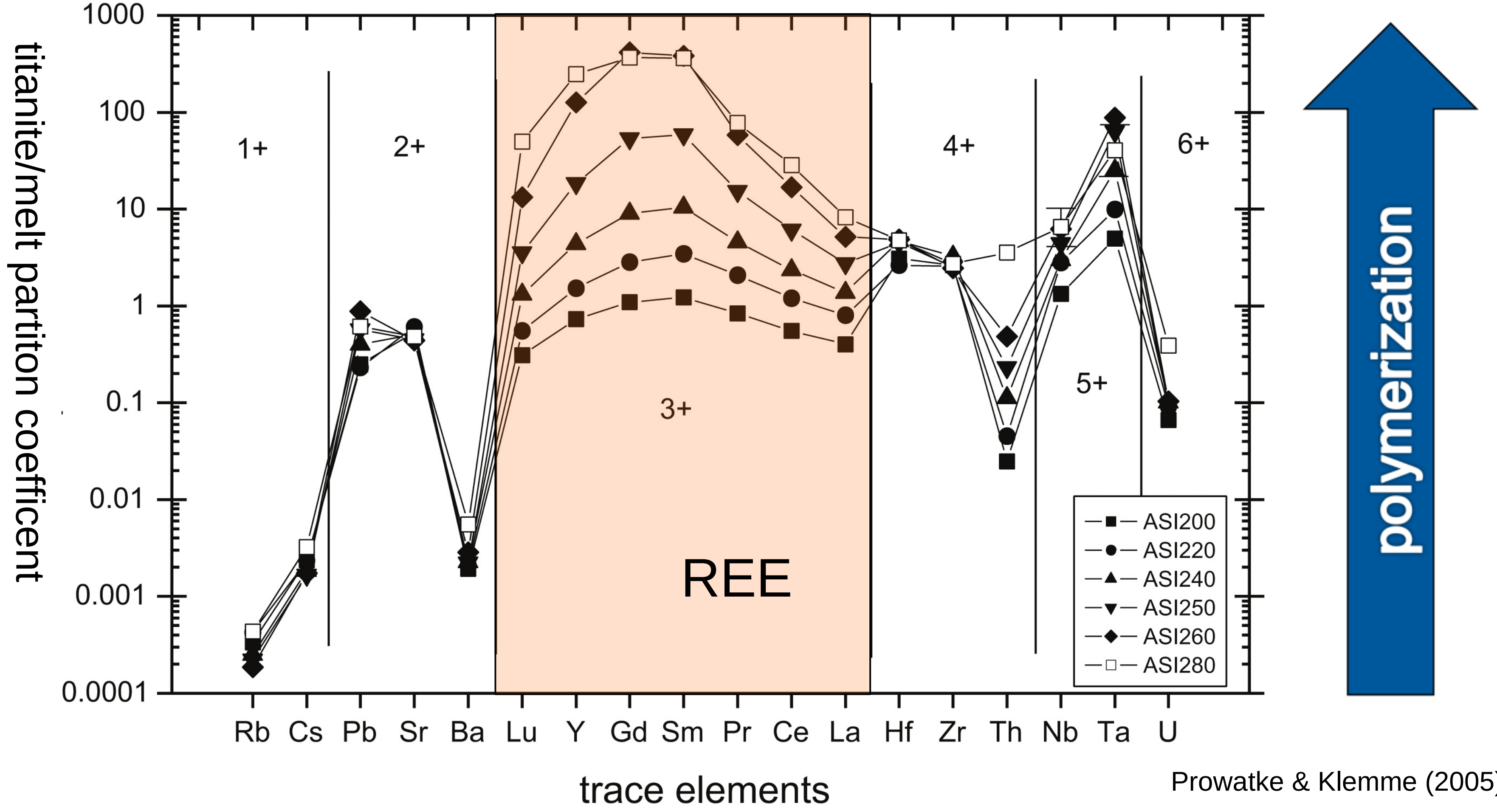
Known Factors:

- temperature
- pressure
- oxygen fugacity
- crystal chemistry

- **melt composition?**

Blundy and Wood (2003)

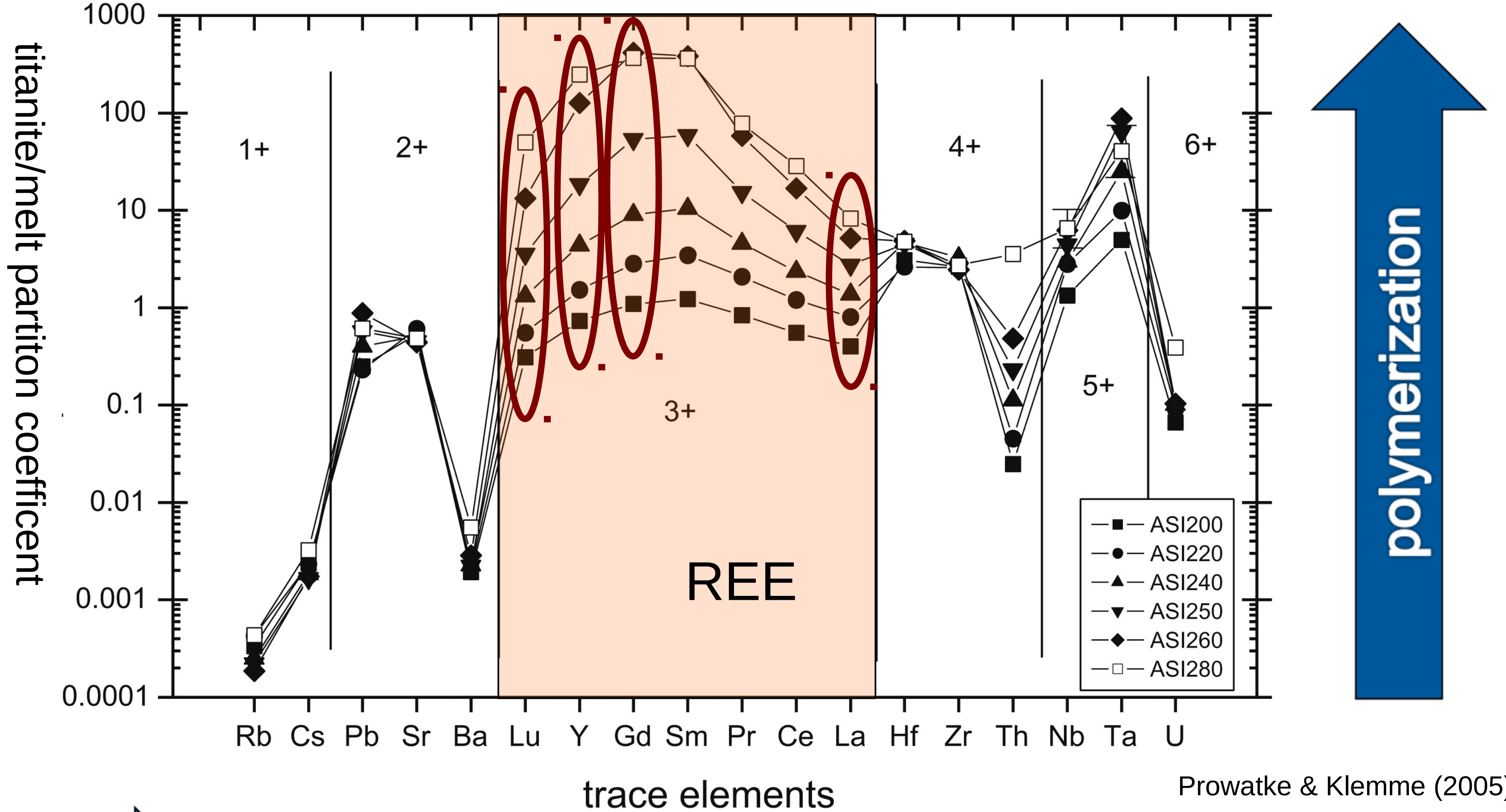
Motivation



Prowatke & Klemme (2005)

- influence of melt composition (polymerization) on the partitioning of trace elements
- all factors (T, p, crystal chemistry) stay nearly constant, only the melt composition change

Studied Trace Elements



Prowatke & Klemme (2005)

AIM **“correlation of trace element partitioning data with local structure environment of trace elements in silicate melts”**

GFZ Helmholtz Centre POTSDAM

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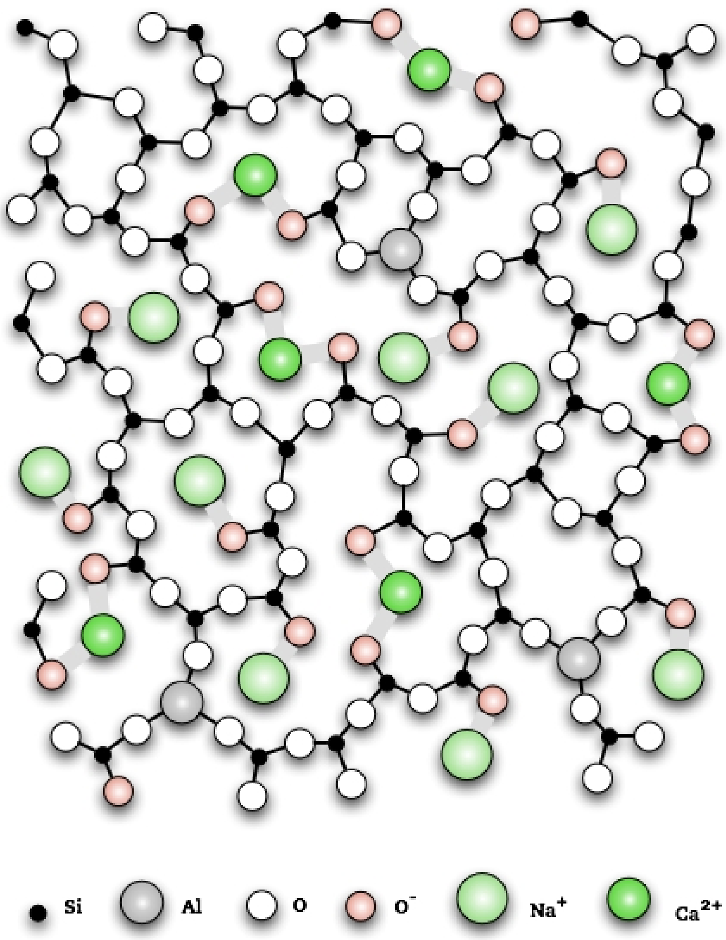
Polymerisation of Glass/Melt



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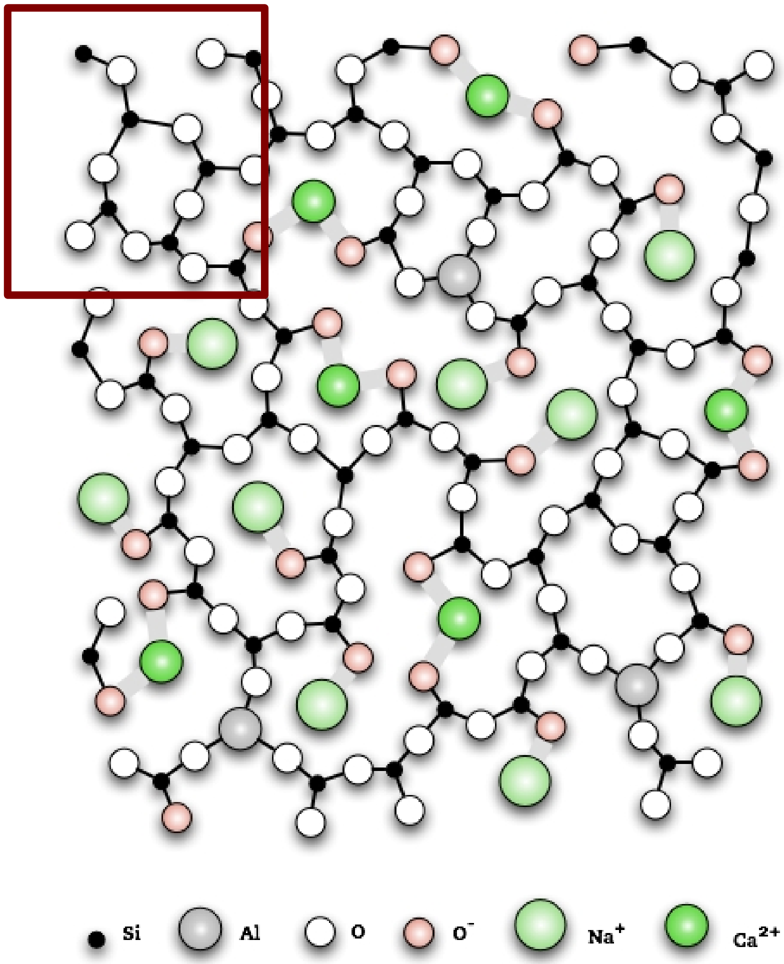
- anionic framework of corner-sharing SiO_4 tetrahedra
- connectivity of the tetrahedra depends on Si/O ratio
- full polymerized network with only bridging oxygens (BO)
- alkaline and alkaline earth cations => depolymerisation; increase of non bridging oxygens (NBO)

- <u>Two different approaches:</u>

  - $NBO/T = 2(NM - T^{3+})/T^{4+}$
  - ASI = molar ratio of Al_2O_3/ (Na_2O + K_2O + C_2O))

Polymerisation of Glass/Melt



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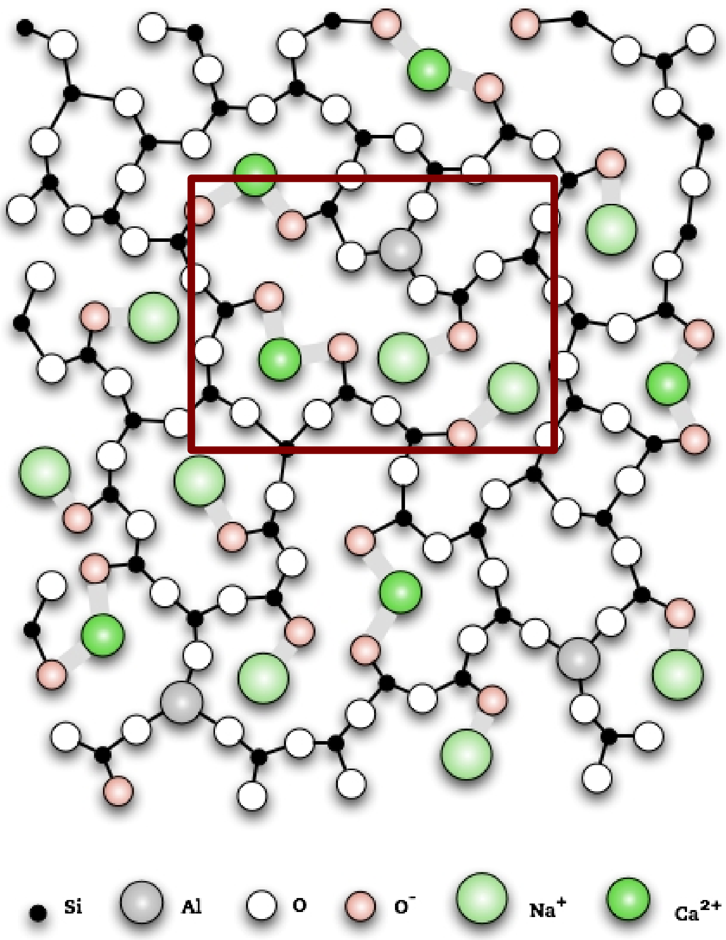

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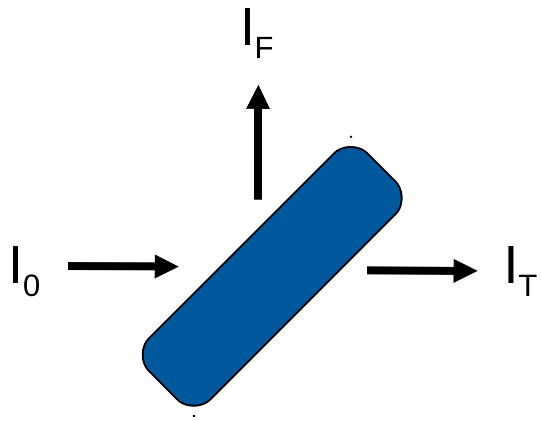
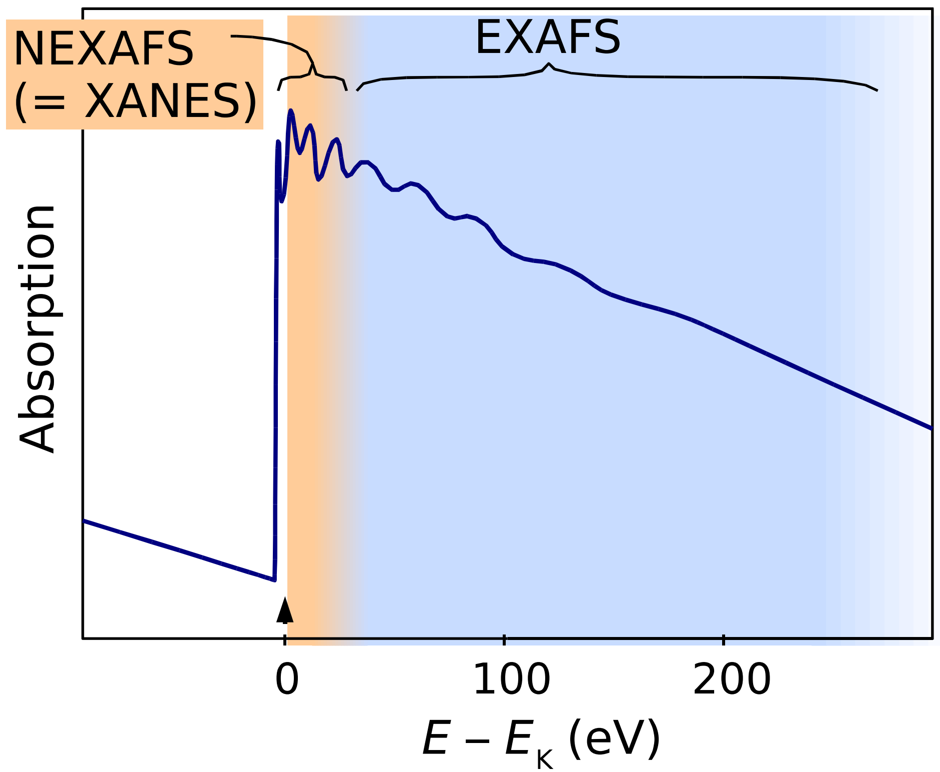
X-Ray Absorption Fine Structure - XAFS



<u>Absorption coefficient:</u>

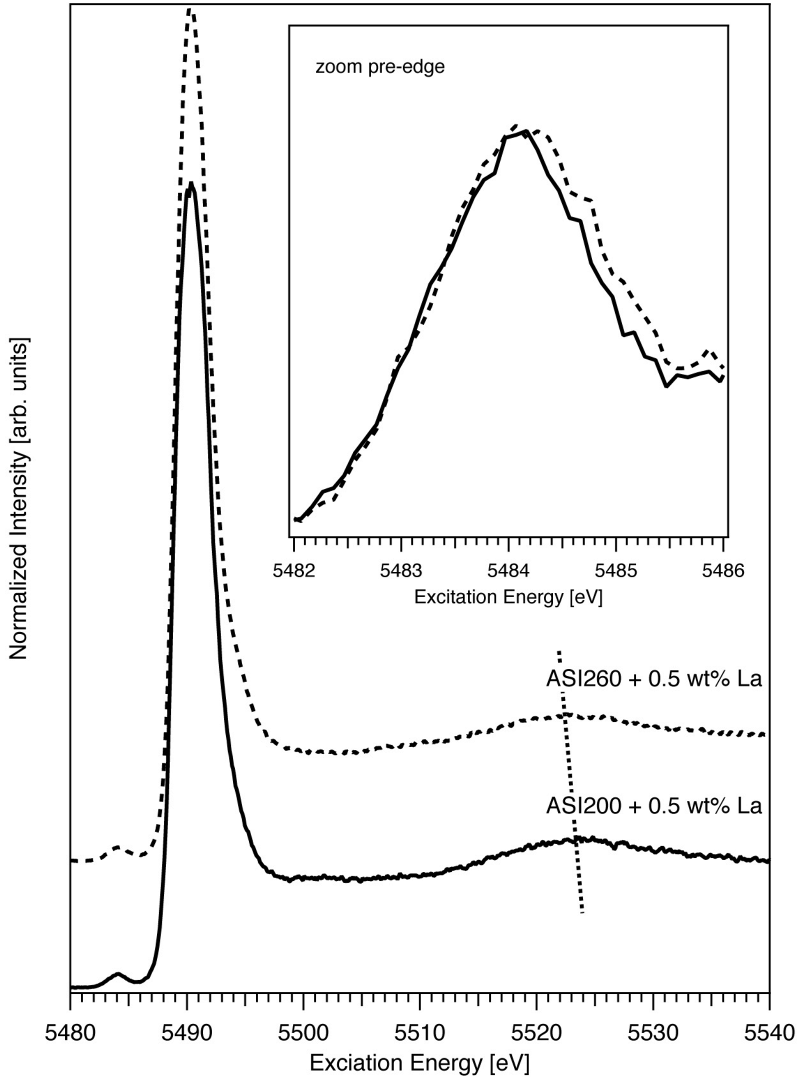
$$\mu(E) = \log (I_0/I_T)$$

$$\mu(E) \approx I_F/I_0$$



- **XANES** = X-ray Absorption Near Edge Structure: coordination- , oxidation change
- **EXAFS** = Extended X-ray Absorption Fine Structure: CN, R, PDF

La L_3-edge – XANES – Glasses



applying Natoli's Rule:

$\Delta E * R^2 = C$

$\Delta E_{ASI200} * R^2_{ASI200} = \Delta E_{ASI260} * R^2_{ASI260}$

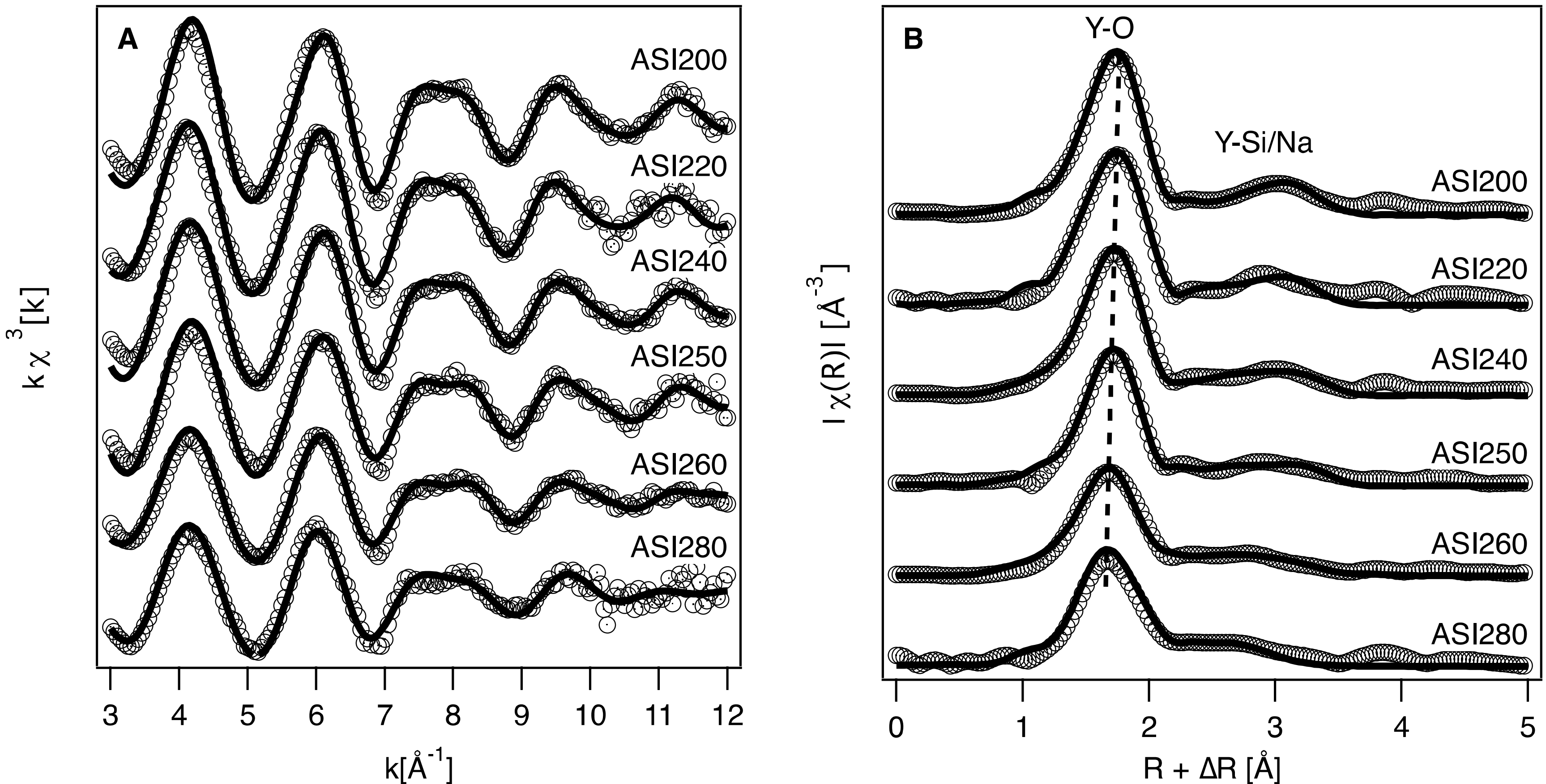
$\Delta E_{ASI260} / \Delta E_{ASI200} = R^2_{ASI260} / R^2_{ASI200}$

$\sqrt{(R^2_{ASI260} / R^2_{ASI200})} = \mathbf{1.02}$

=> bond length La-O increase from ASI200 to ASI260 for 2%

Simon et. al. (in. prep.)

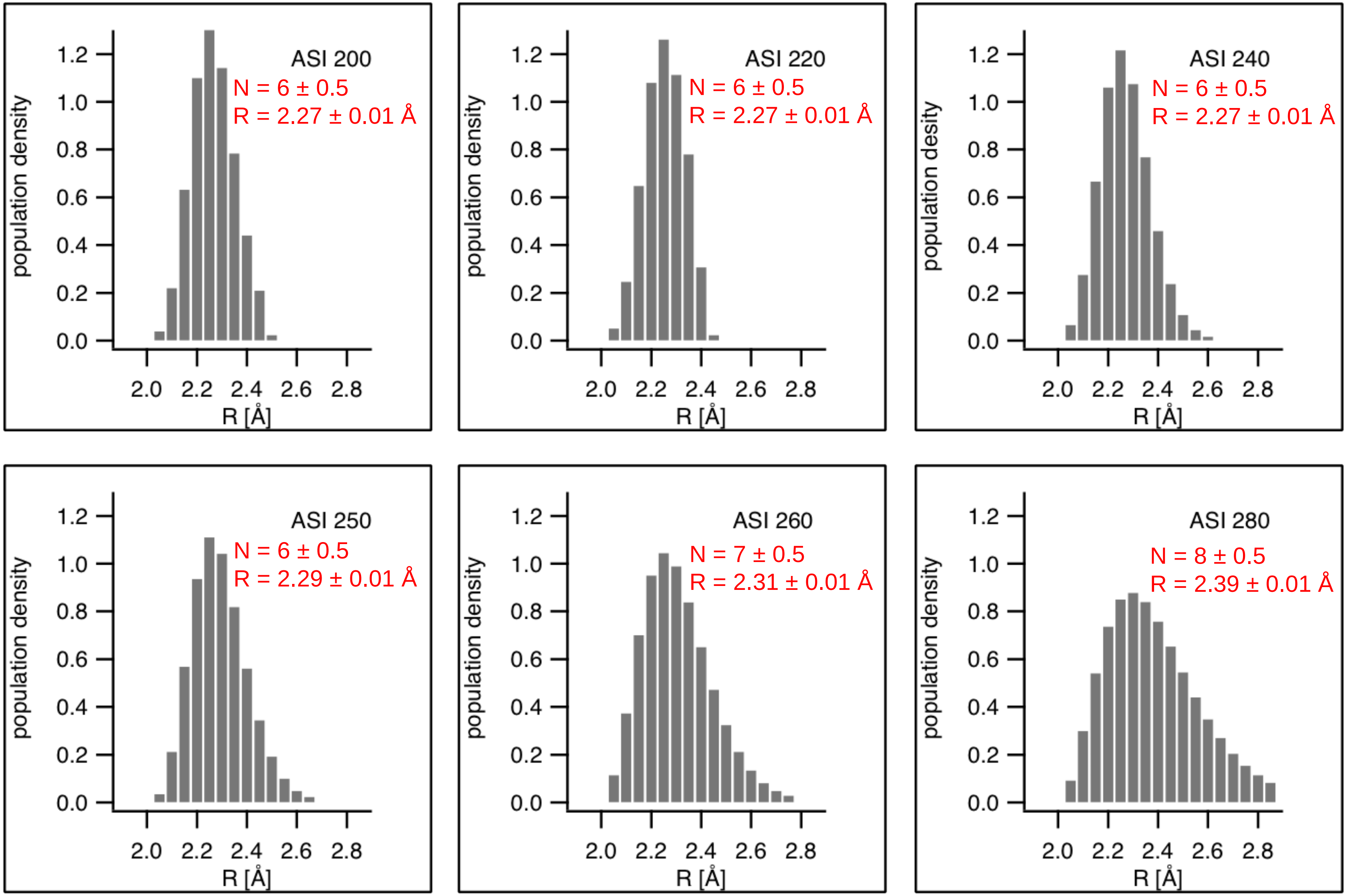
Y K-edge – EXAFS - Glasses



Simon et. al. (2012)

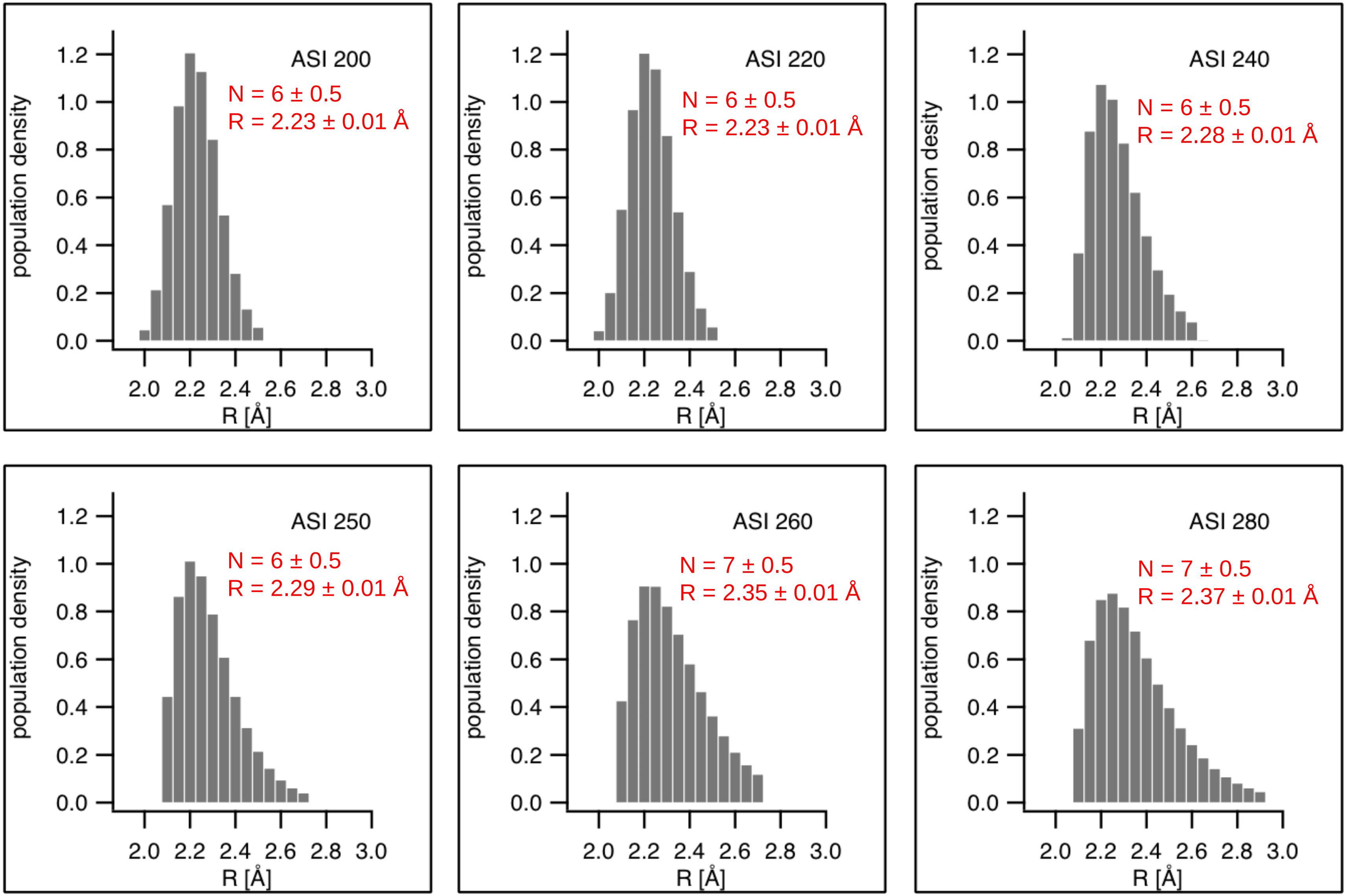
- k^3- weighted oscillations and Fourier transformations of the EXAFS
- glasses with increasing ASI (polymerization) from ASI200 => ASI280

Y-O Pair Distribution Function

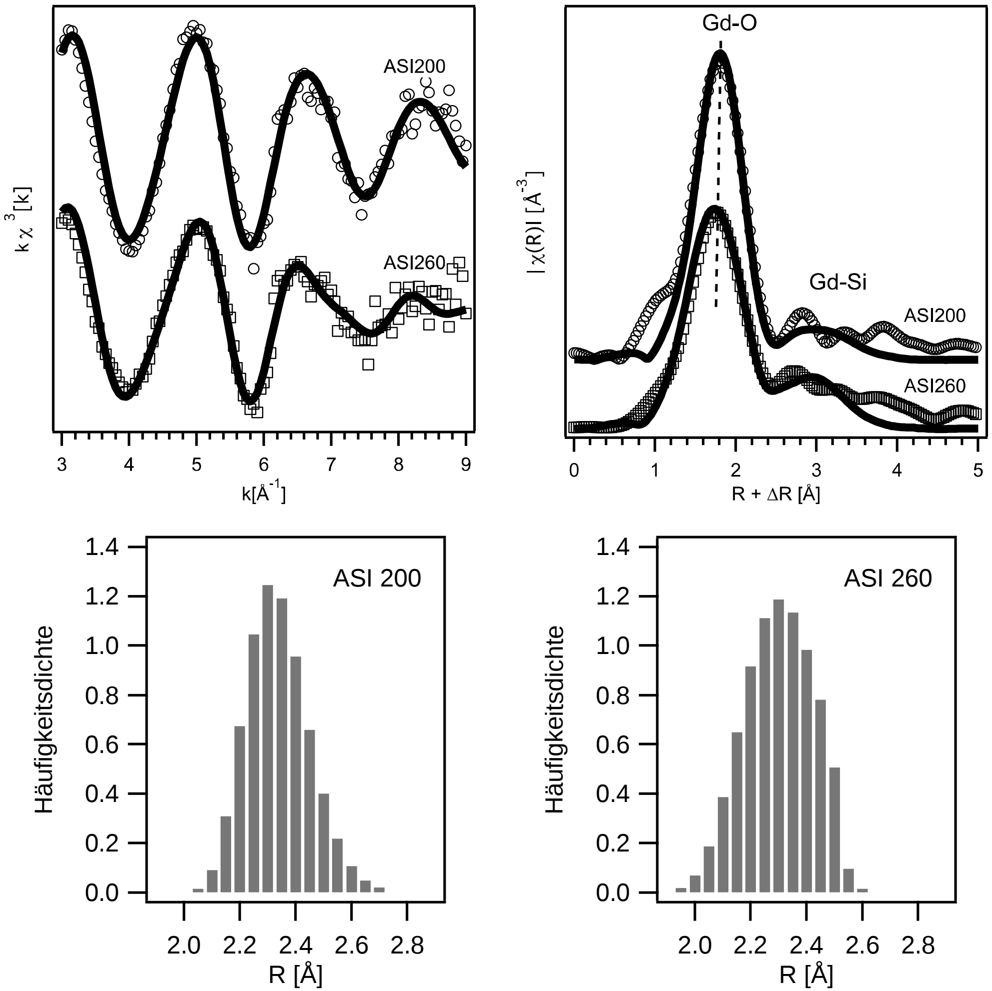


Simon et. al. (2012)

Yb-O Pair Distribution Function



Gd-O Pair Distribution Function

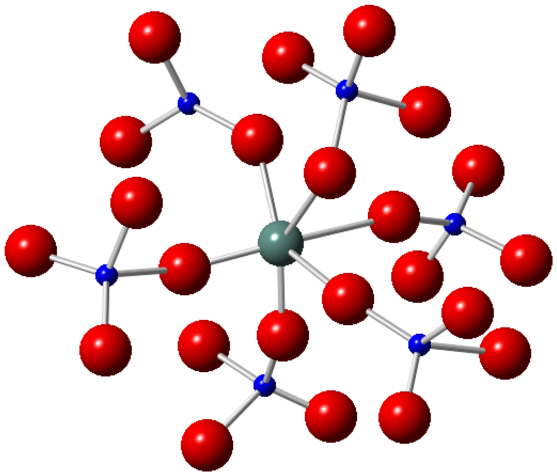


N = 7 ± 0.5
R = 2.34 ± 0.01 Å

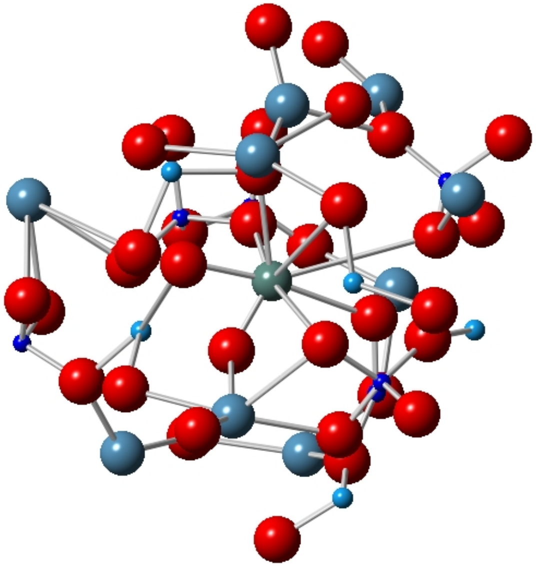
N = 9 ± 0.5
R = 2.39 ± 0.01 Å

Simon et. al. (in. prep.)

None Bridging Oxygen's vs. Bridging Oxygen’s



depolymerized melt



polymerized melt

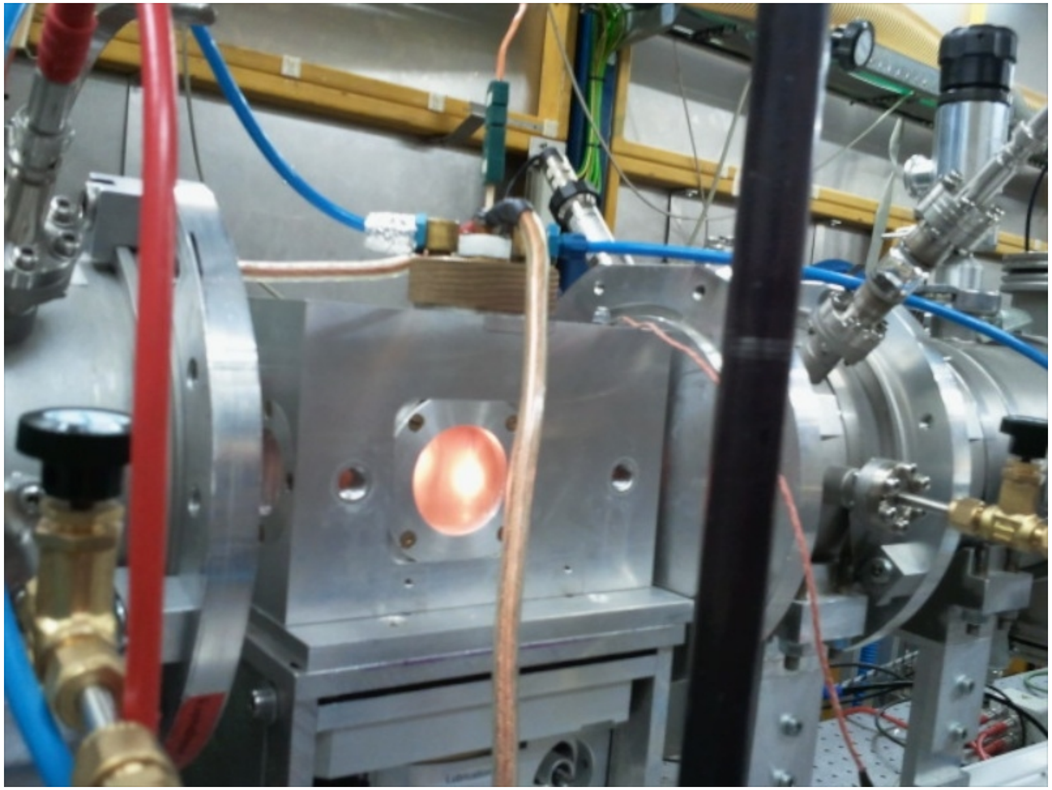
- less polymerized melt => number of NBO’s high enough => **symmetric PDF**
- more polymerized => not enough NBO’s available, over-bonding of BO’s counterbalanced by an increase of CN and R => **broad and asymmetric PDF**

Correlation of D with R?

REE	R_{ASI260}/R_{ASI200}	D_{ASI260}/D_{ASI200}
La	1.02	12.9
Gd	1.01	381.7
Y	1.01	172.6
Yb	1.03	42.6

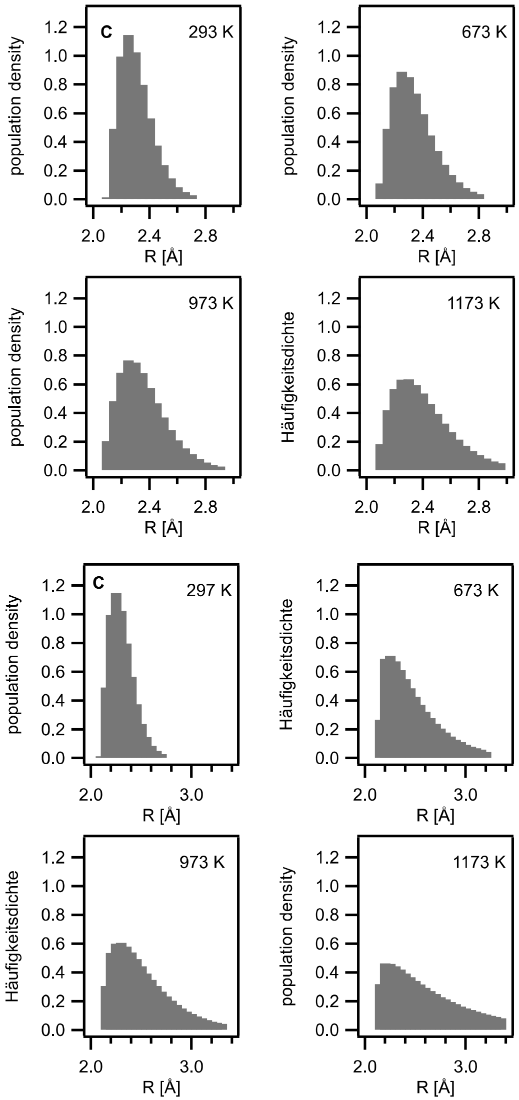
- increase of radial distance REE-O of ≈ 1-3%
- 6-fold coordination is more favourable
- strong correlation of the D with R

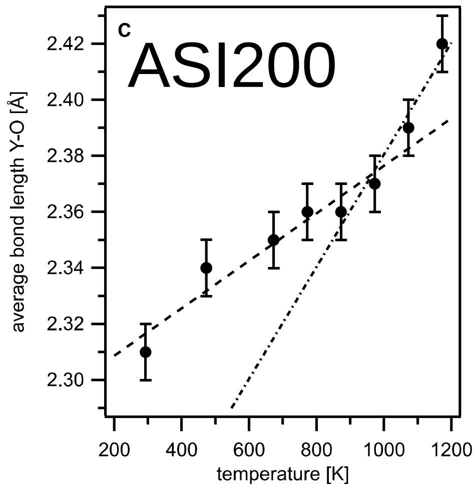
Glass Structure = Melt Structure?

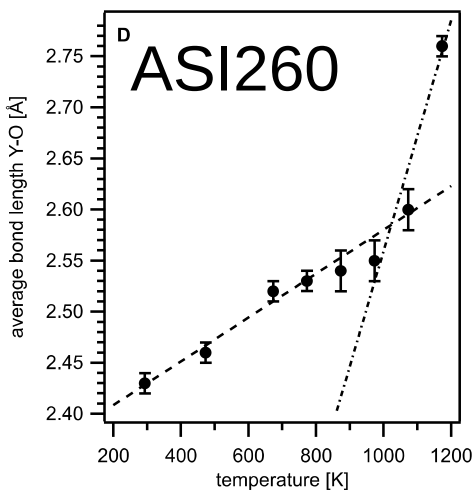


- proof if structure above T_G correspond to structure in quenched melts
- in situ EXAFS measurement from room temperature up to 900°C under atmospheric conditions
- glasses were heated with $PtRh_{10}$-loop and fluorescence was collected

HT Y-EXAFS – Glass/Melt







- PDF getting skewer and broader with increase of T
- increase of R with thermal expansion of glass/melt
- change in slope indicate T_G
- small changes of coordination from glass to melt, reflected in R
- change of the coordination number within the uncertainties of the method

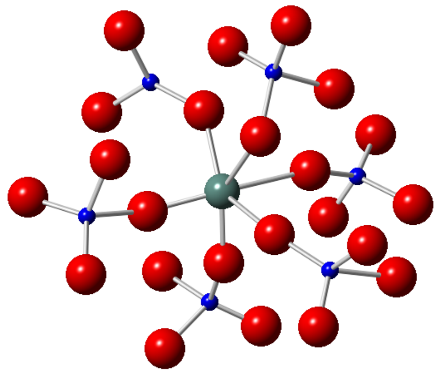
Simon et. al. (in. prep.)

Summary

- **6-fold coordinated REE** will preferentially bond to **NBO's**
- **over-bonding of BO's** around REE is counterbalanced by an **increase** of **coordination number and distance** to satisfy local charge balance requirements => **increase in asymmetry and width of distribution**
- **strong correlation** between $D_{titanite/melt}$ and R => more complex
- **small changes** of local structure of REE between **glass and melt**

<u>Take Home Message:</u>

•configuration in **less polymerized melts** are more favorable than the one in polymerized melts => this makes the **REE more compatible** in these melts



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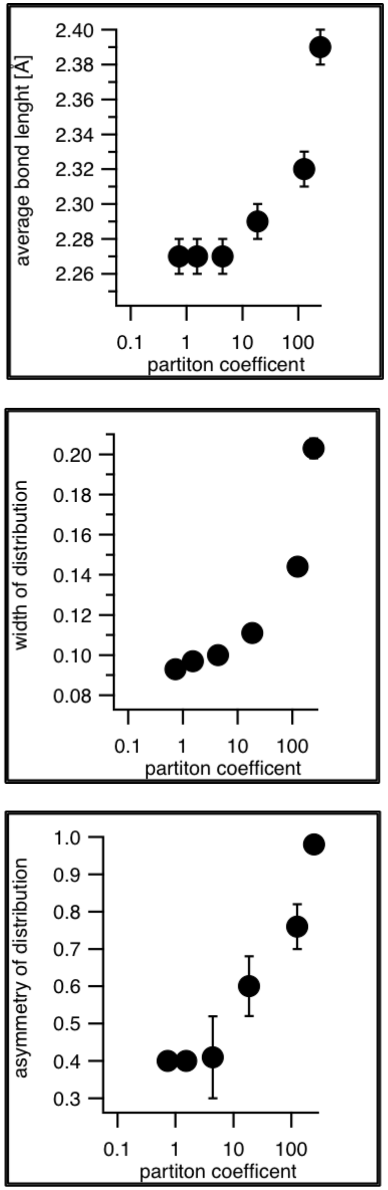

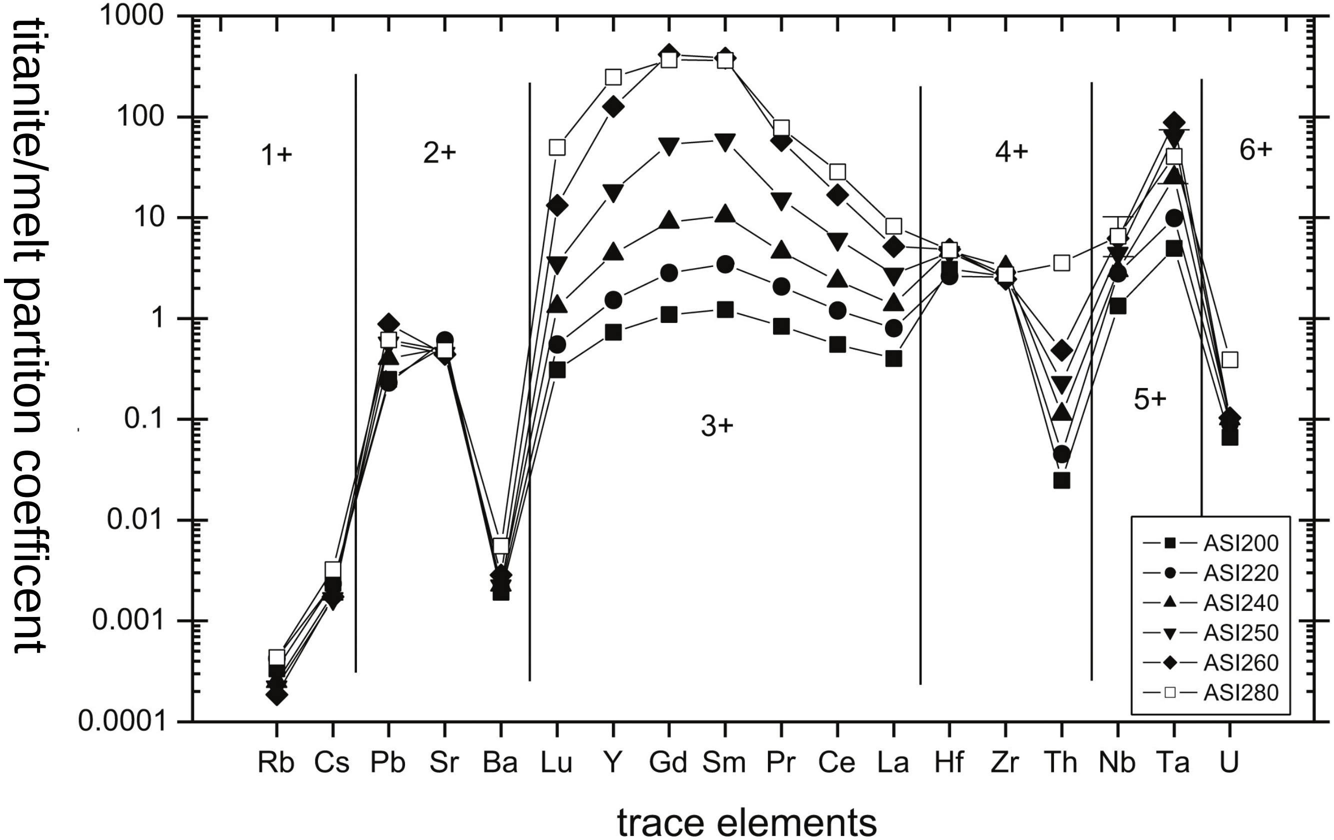

Further informations: Simon, Wilke, Chernikov, Klemme & Hennet (2012) Chem. Geol.