

Structure of carbonate-silicate melts and quench glasses and speciation of Y, Sr, Zr

A. SHIRYAEV, A. AVERIN, M. NICKOLSKY – Institute of physical chemistry and electrochemistry
RAS, Moscow

V. MURZIN, A. VELIGZHANIN, Y. ZUBAVICHUS - Kurchatov Institute, Moscow

O. SAFONOV, V.O. YAPASKURT – MSU, MOSCOW

O. MATHON - ESRF, Grenoble

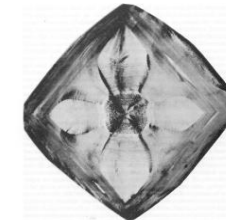
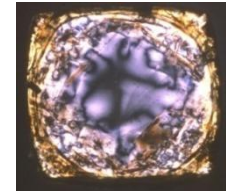
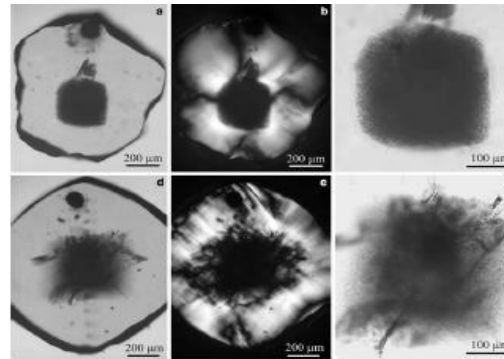
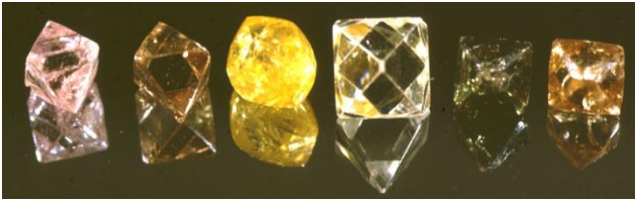
J. POHLENZ, M. WILKE - GFZ, Potsdam

T. Irifune – Ehime University

Scientific motivation

- Structure of carbonate-silicate melts – a clue to understand their properties and behaviour, especially isotopic and chemical fractionation processes. Challenge for physics and chemistry due to complexity.
- Strontium is interesting on its own (Sr carbonate is present as inclusions in fibrous diamonds) and may serve as a proxy for Ca.
- Y is a proxy for REE.

- Formation of diamonds.



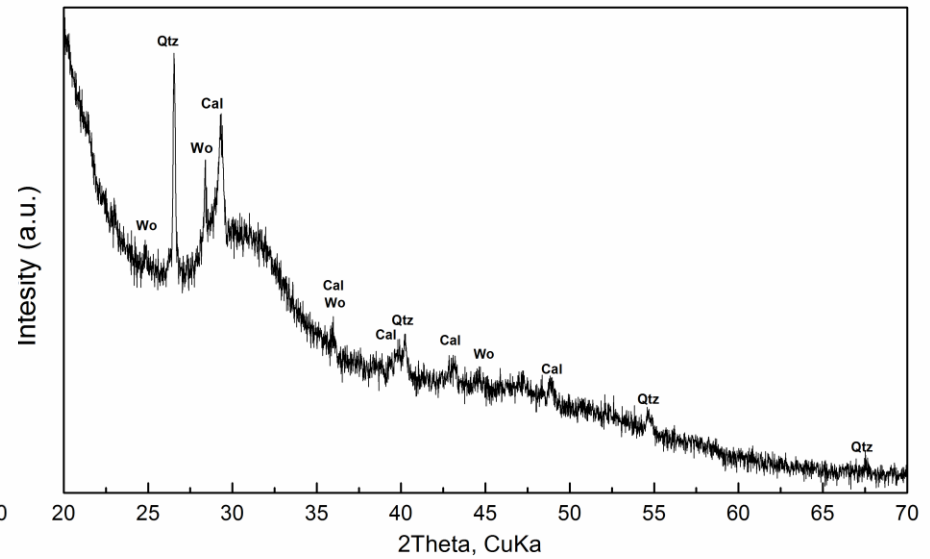
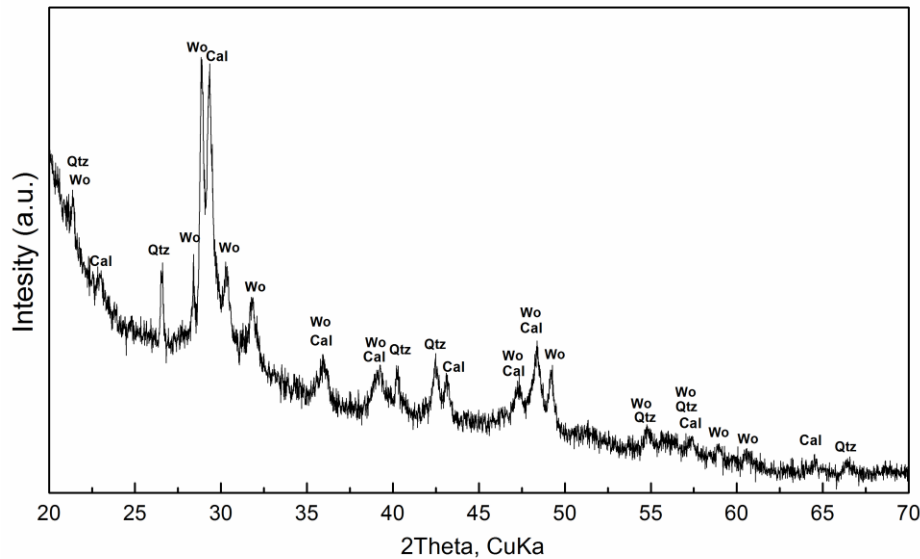
- Formation of large-scale deposits of Rare-Earth elements, Nb, Ta

Methods and samples

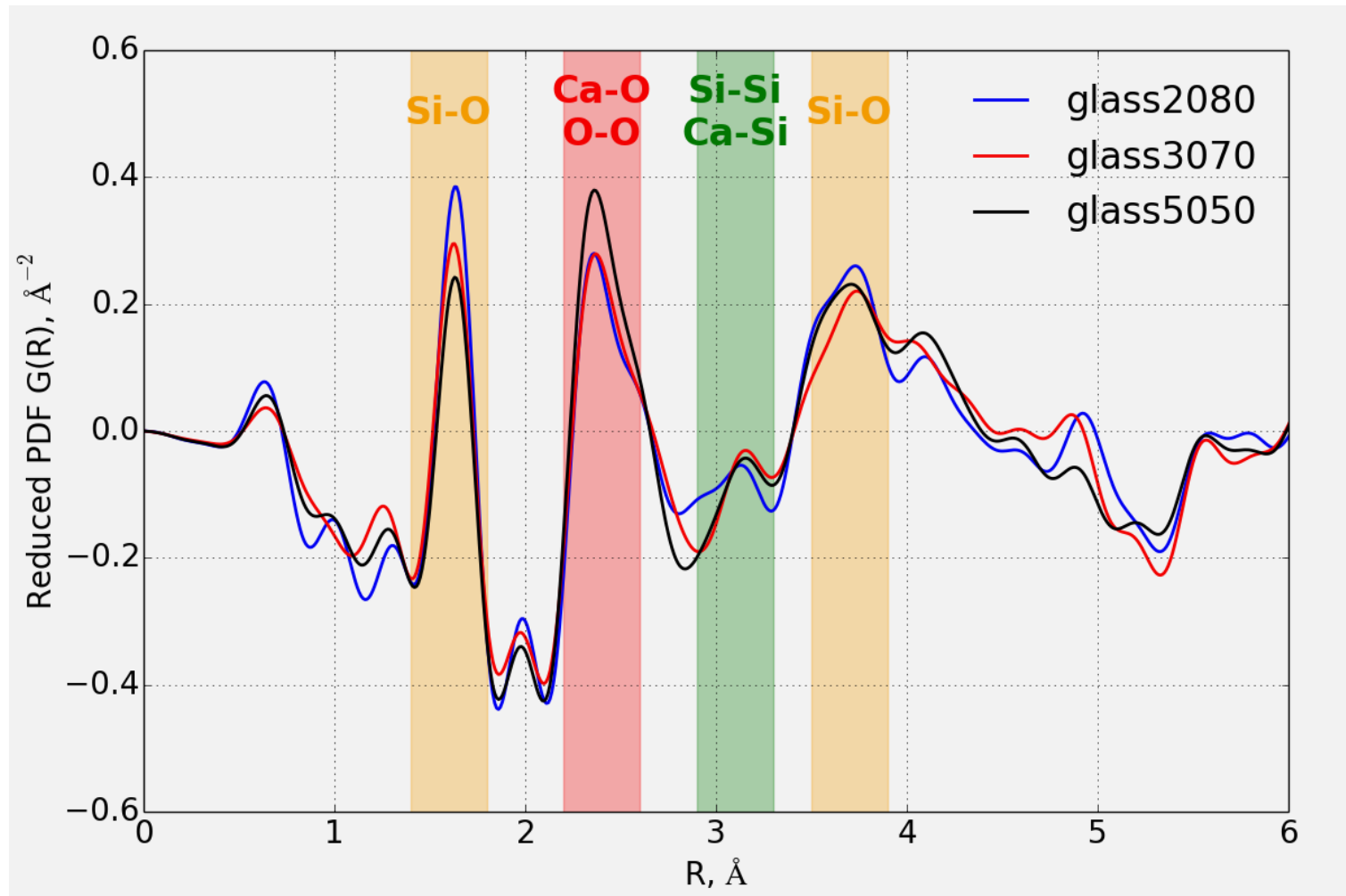
- $\text{CaSiO}_3 + (\text{CaCO}_3 \pm \text{Na}_2\text{CO}_3)$ in various ratio (from 90:10 to 50:50) + $\text{SrCO}_3 + \text{Y}_2\text{O}_3 + \text{ZrO}_2$ (<0.5%)
- Ex-situ: HPHT treatment at 4-5.5 GPa – 1500-1700 °C
- In situ: Paris-Edinburgh press, 2-5 GPa – 1200-1700 °C
- XAFS at Sr, Y, Zr, Nb K-edges (ESRF, Soleil, KCSR)
- XRD and High-Energy XRD (PETRA III)
- Microprobe
- TEM
- Micro-Raman and micro-IR (in reflection geometry)

X-ray Diffraction (ex situ)

- No traces of initial Sr-Y-Zr compounds (carbonates/oxides)
- Samples consist of silicate glass, calcite (domain size 15-30 nm) +/- minor SiO₂ and residual wollastonite.

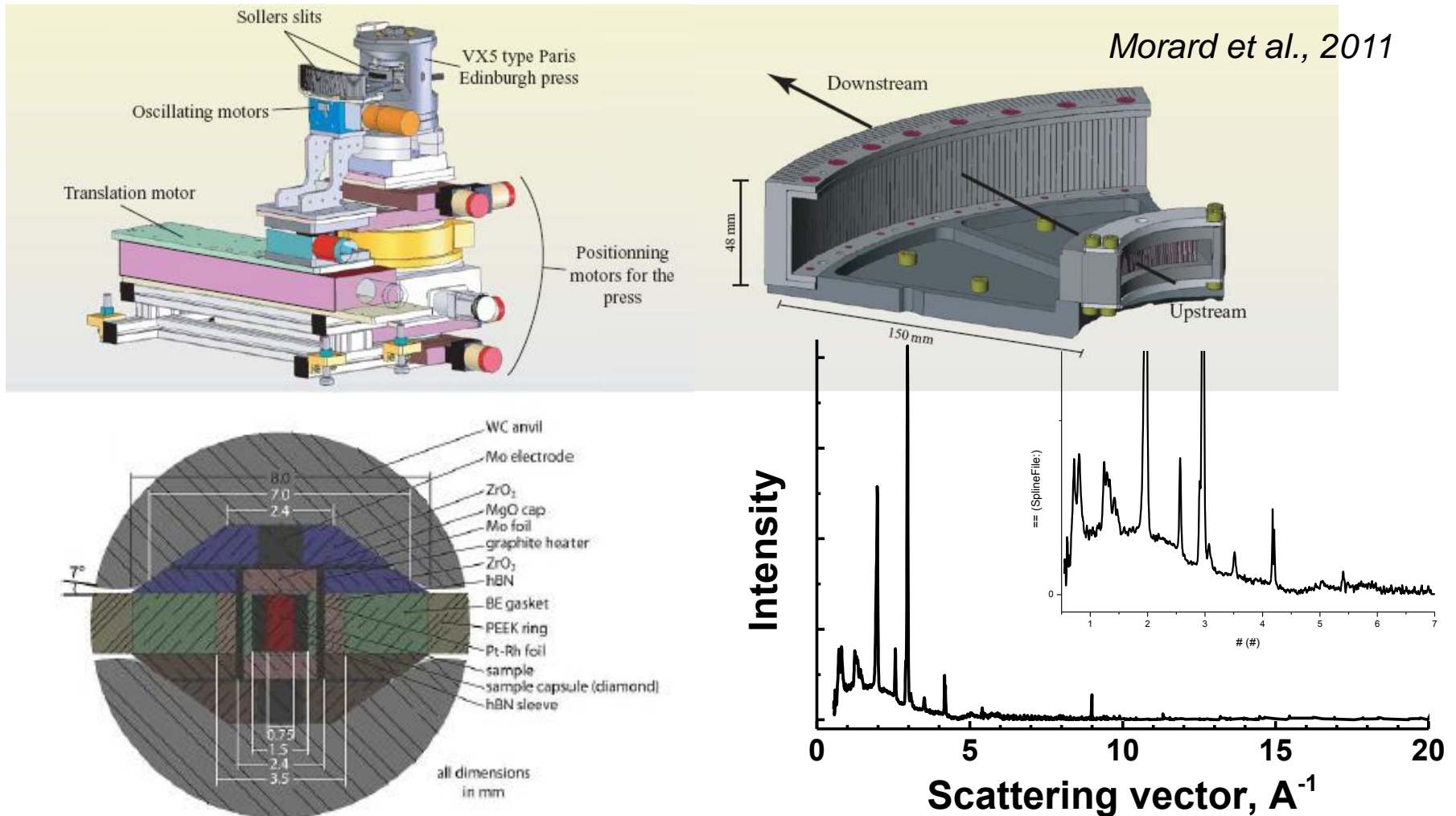


Pair distribution function analysis (ex-situ)

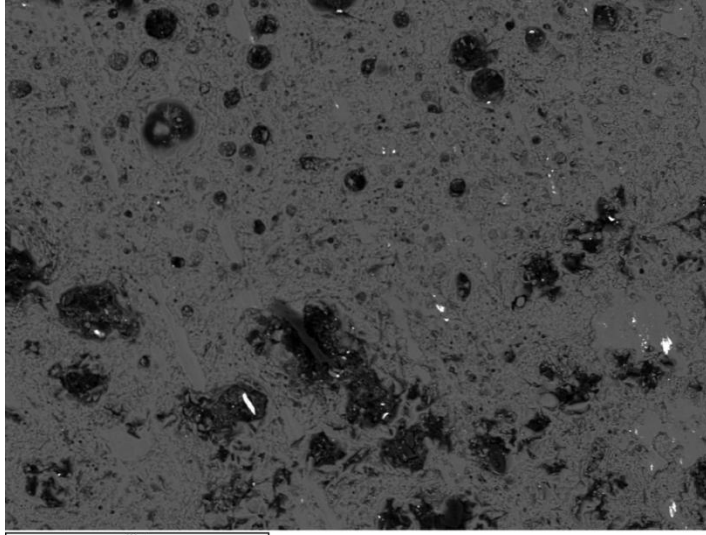


X-ray Diffraction (in situ)

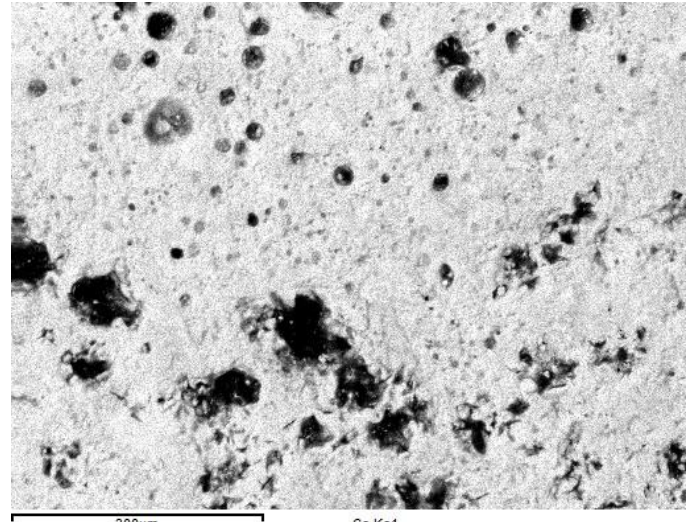
We have commissioned the Paris-Edinburgh press at P02.1 beamline at PETRA III synchrotron in Hamburg.



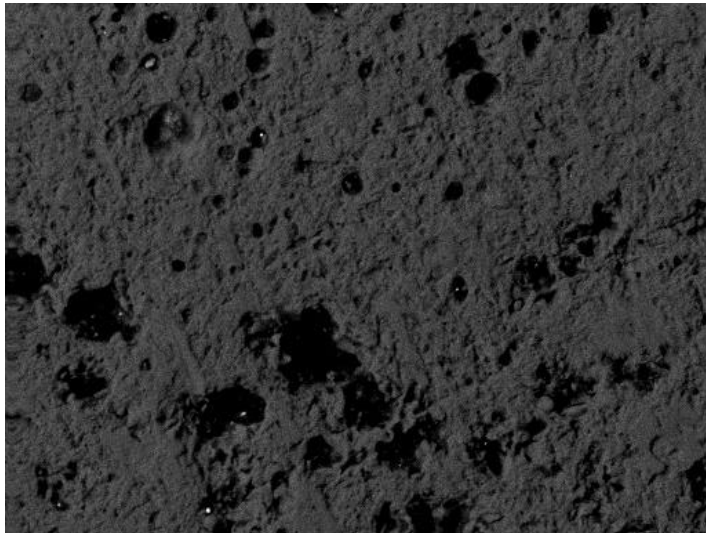
Elemental mapping of quench samples



BSE image



Ca map



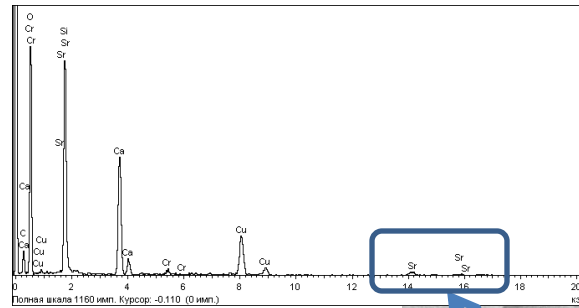
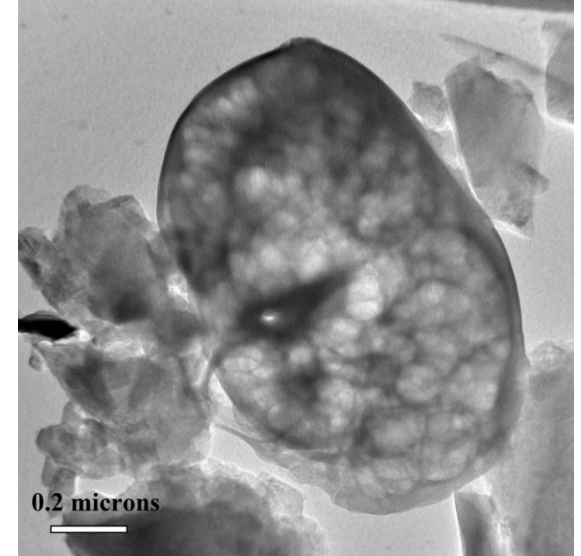
Si map



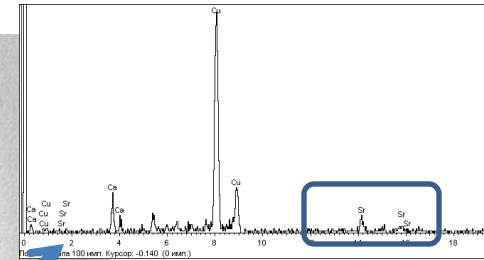
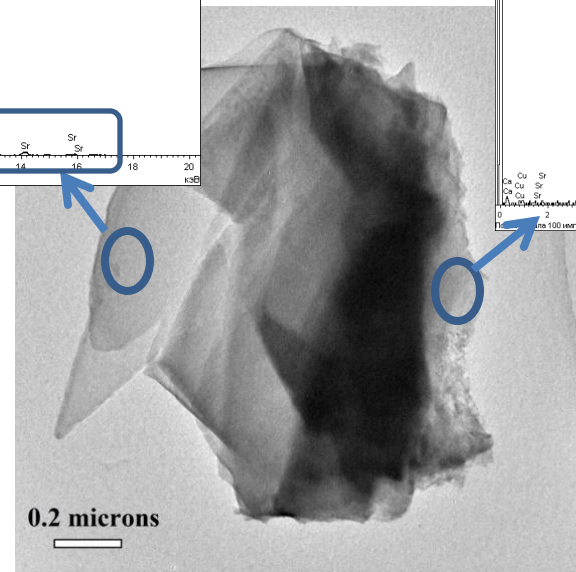
Sr map

Transmission Electron Microscopy

- Vigorous reaction of many observed carbonate chips under the e-beam indicate that decarbonatisation at HPHT was not strongly pronounced

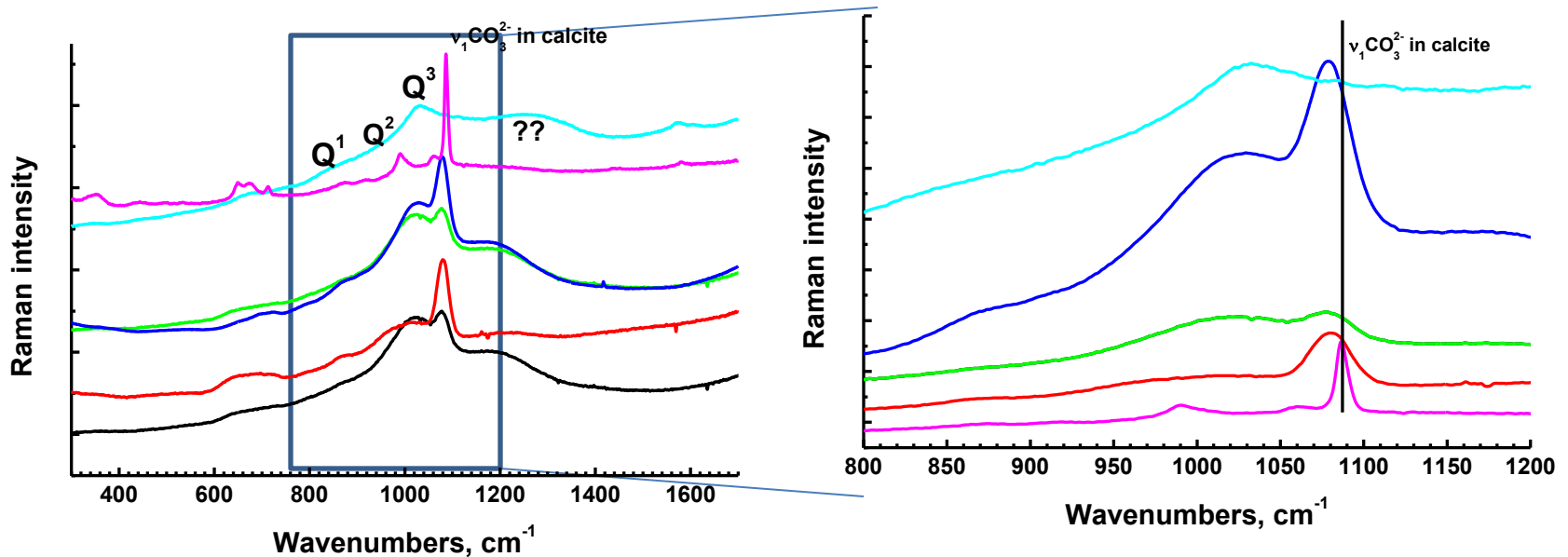
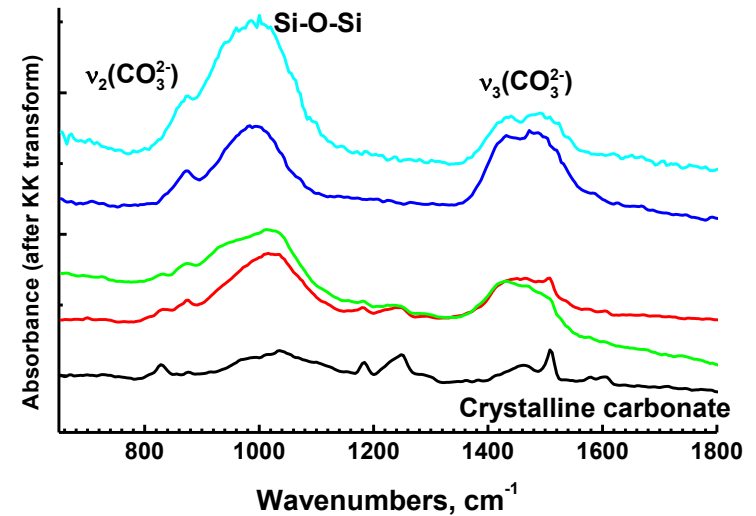


- Sr partitions between carbonate and silicate phases



Vibrational spectroscopy (ex-situ)

- IR and Raman show presence of sharp carbonate (CO_3^{2-}) peaks and broad features.
- The carbonate phase does not coincide with pure calcite (its presence follows from XRD)
=>
 - Impurities/defects shift peaks' positions
 - the "dissolved" CO_2 peak position changes with glass density (Morizet et al., 2013)

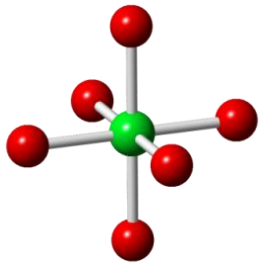


X-ray Absorption Spectroscopy

In quench samples Sr, Y and Zr may partition between (at least) two phases: silicate glass and carbonate => consistent fitting of XAFS is difficult.

Histogram fits were attempted. Strong influence of background subtraction.

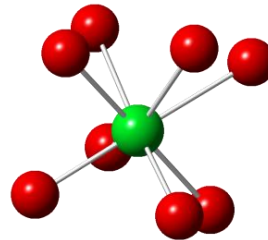
CN = 6



Sr in SrO(cryst.)
6x~2.56Å

Y in Y₂O₃(cryst.)
6x~2.29Å

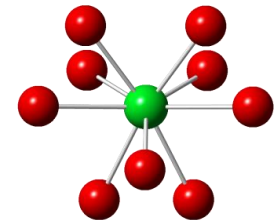
CN = 8



Sr in SrSiO₃(cryst.)
2x~2.45Å
4x~2.69Å
2x~2.74Å

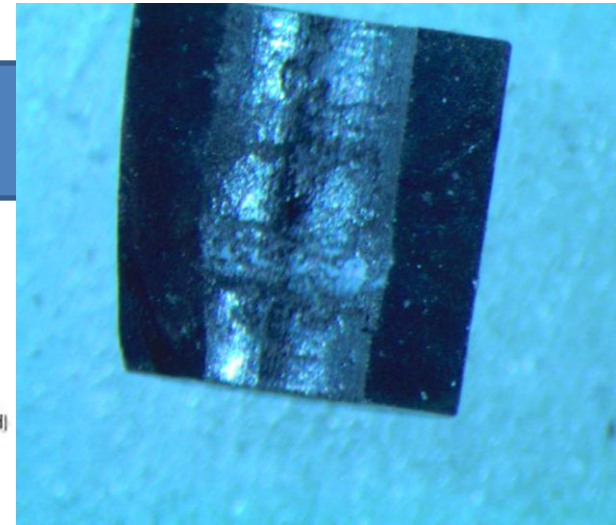
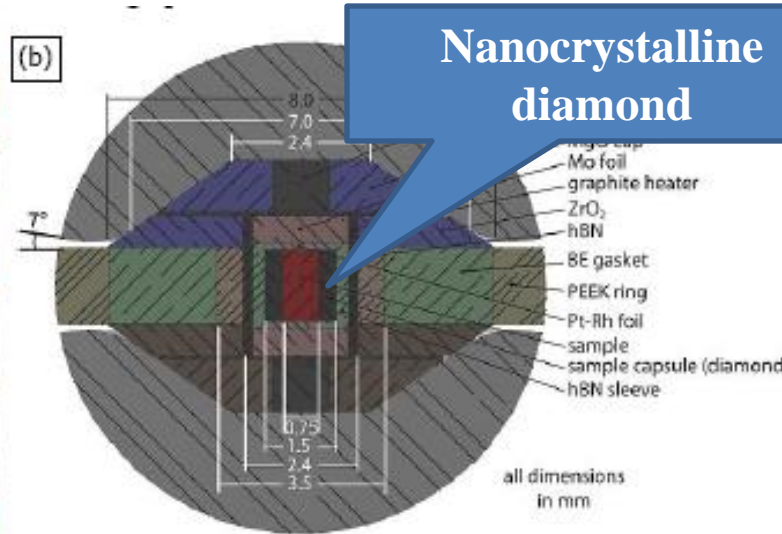
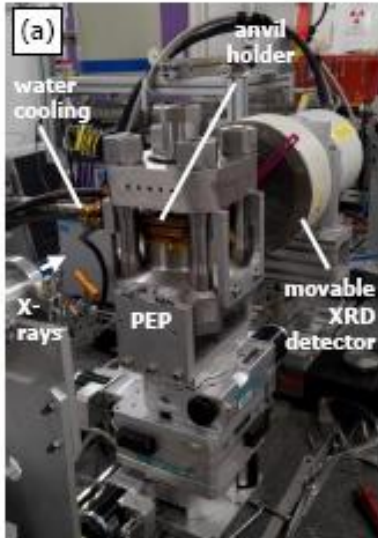
Y in Y₃Al₂(AlO₄)₃(cryst.)
4x~2.33Å
4x~2.46Å

CN = 9

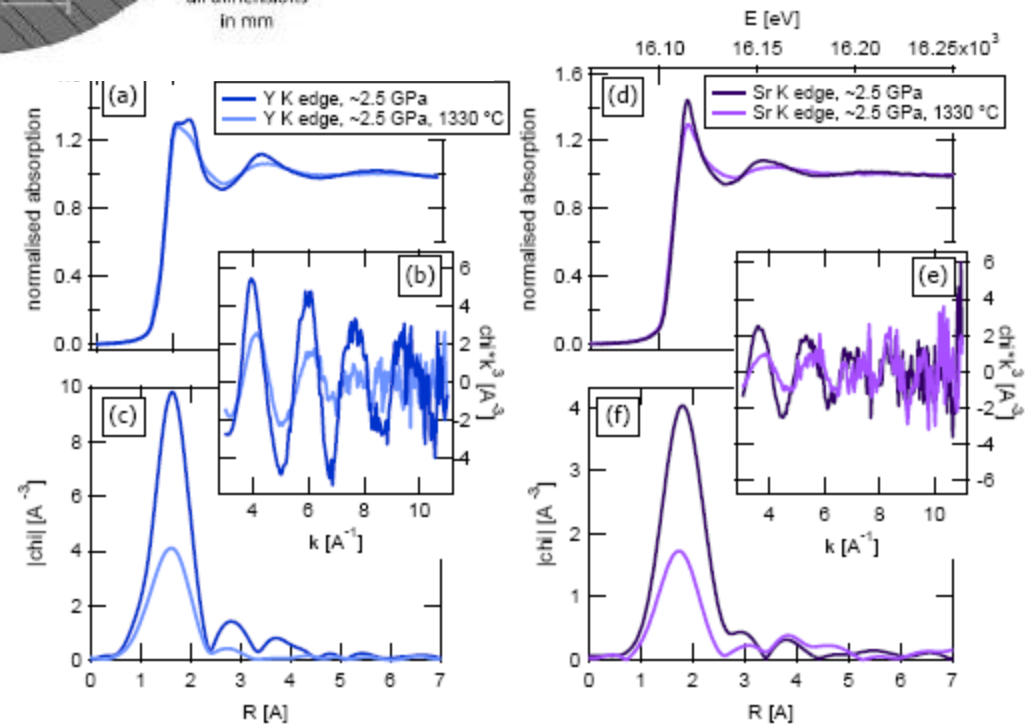


Sr in SrCO₃(cryst.)
3x~2.55Å
2x~2.64Å
2x~2.67Å
2x~2.73Å

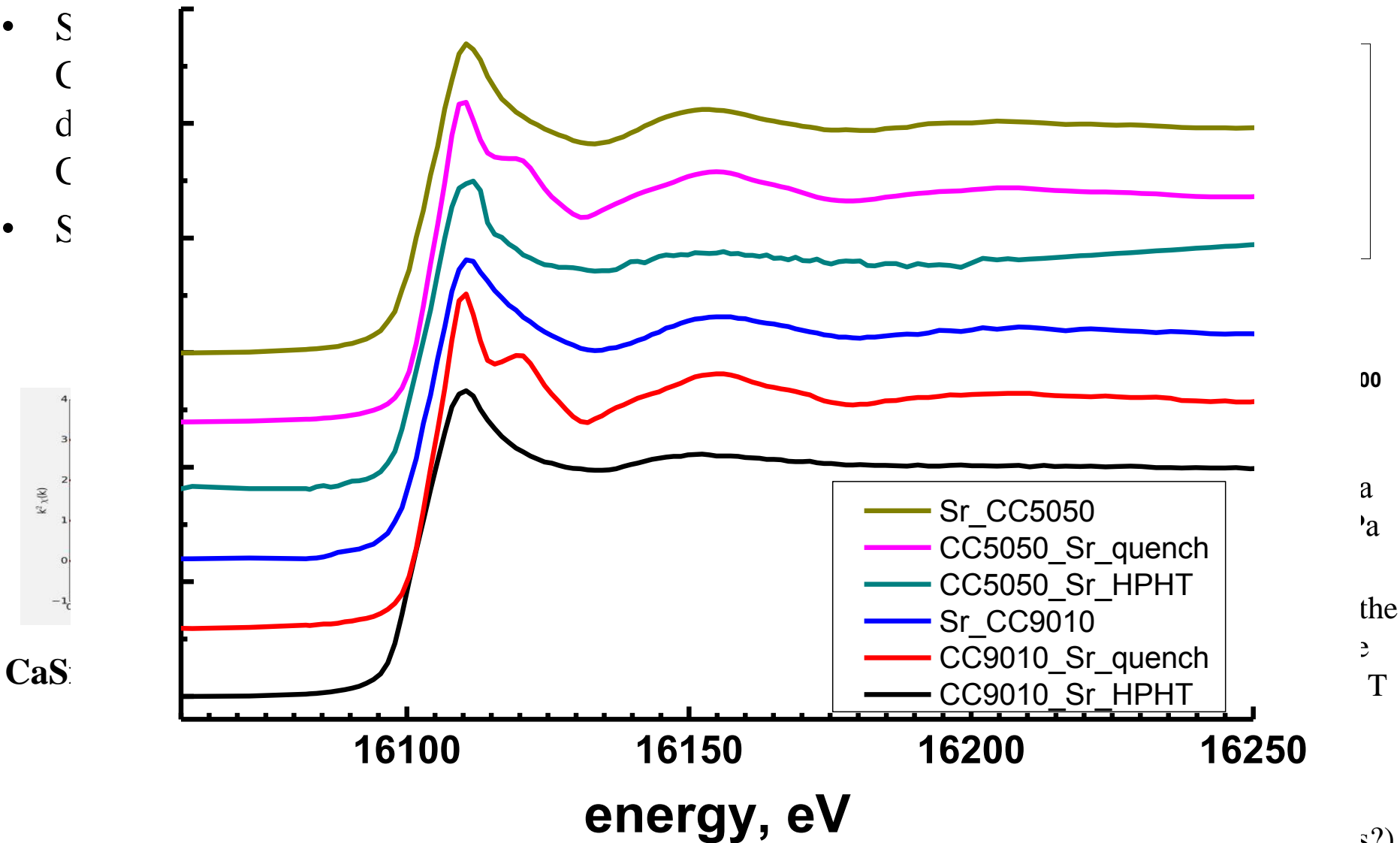
XAFS in situ



System with <10% CO₂

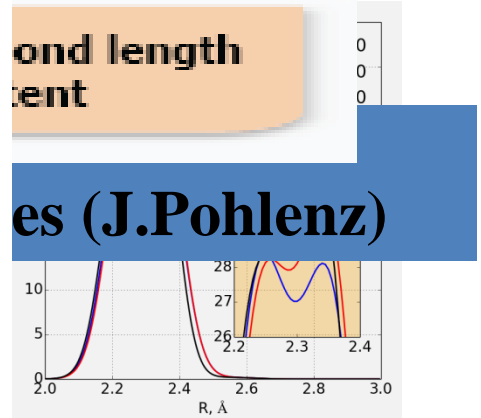
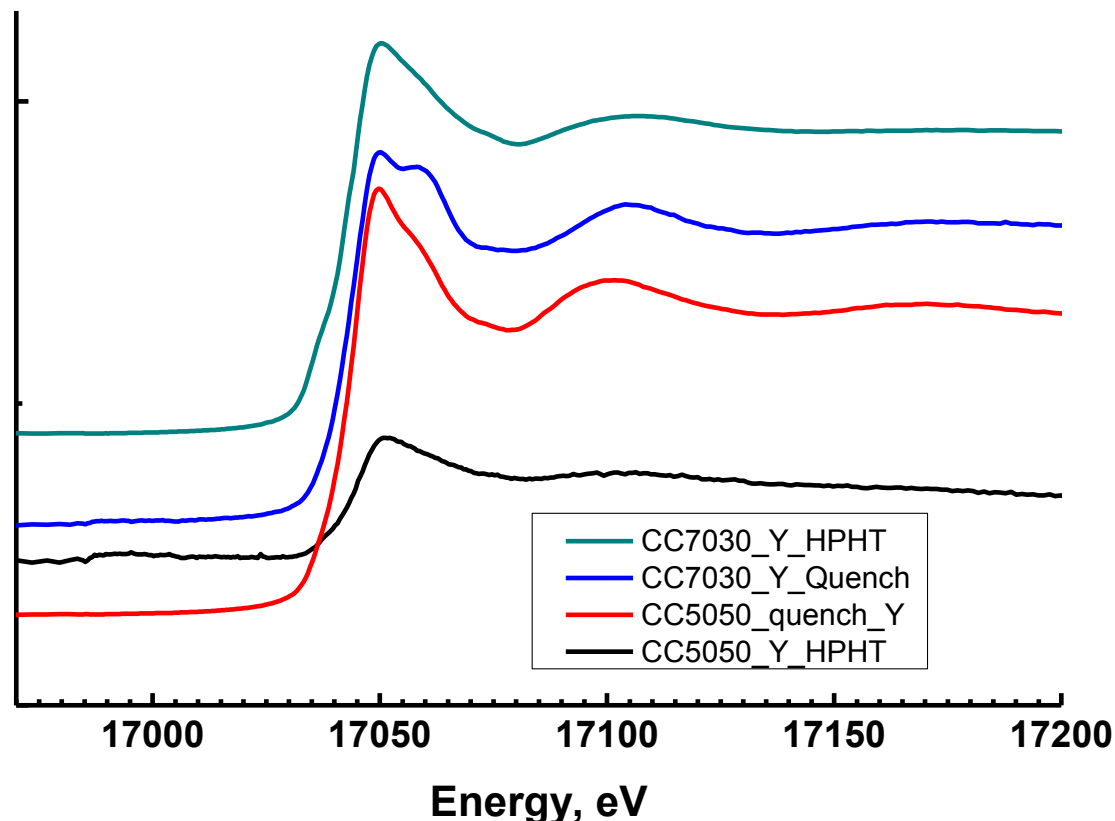
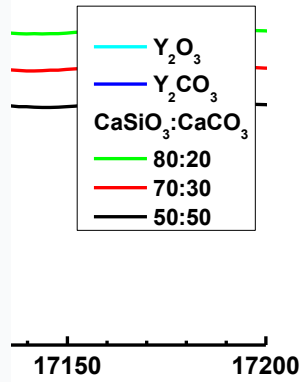
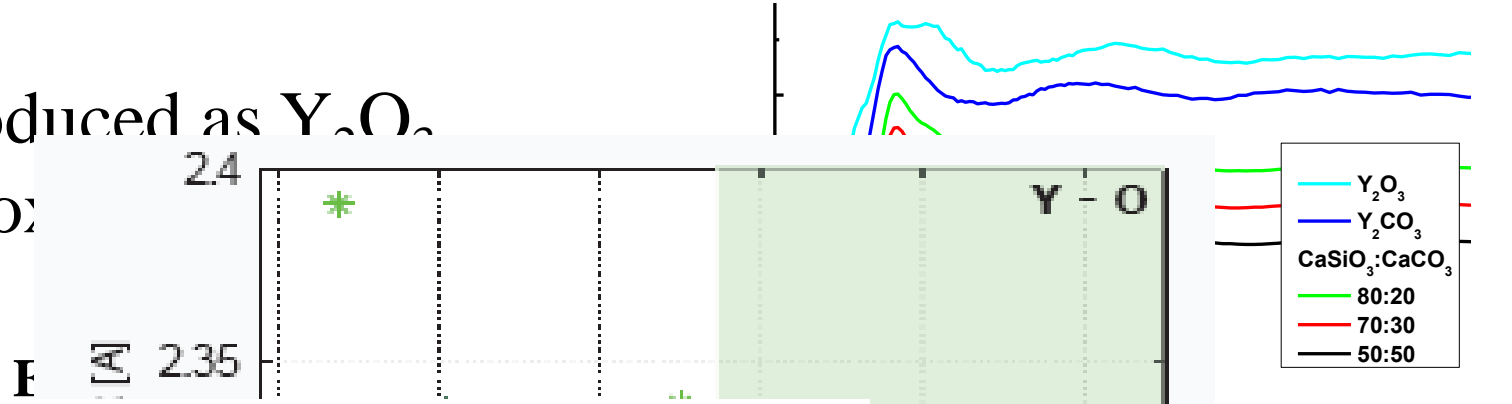


Strontium XAFS



Yttrium XAFS

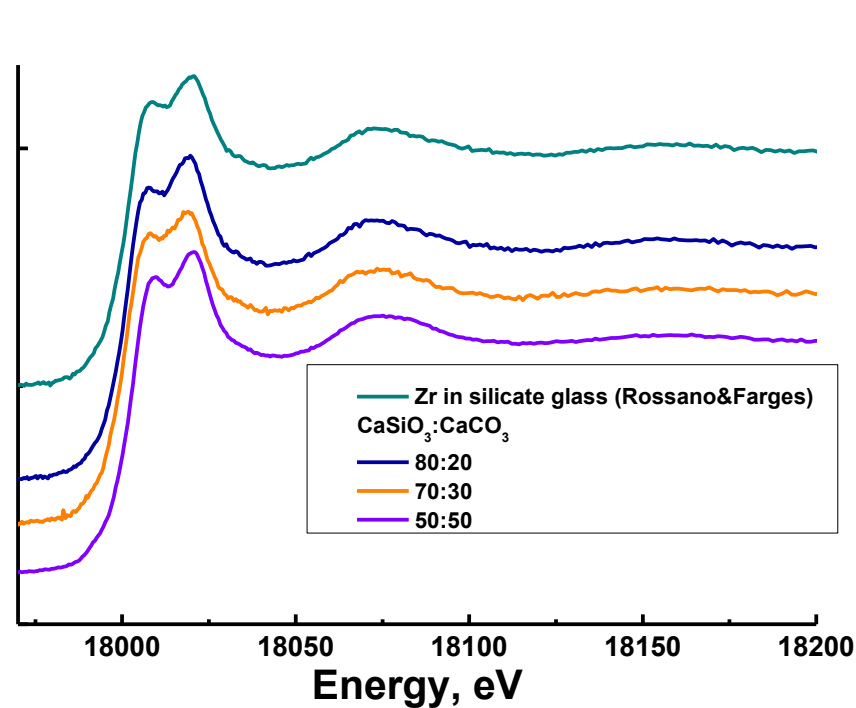
Y was introduced as Y_2O_3
 Starting on



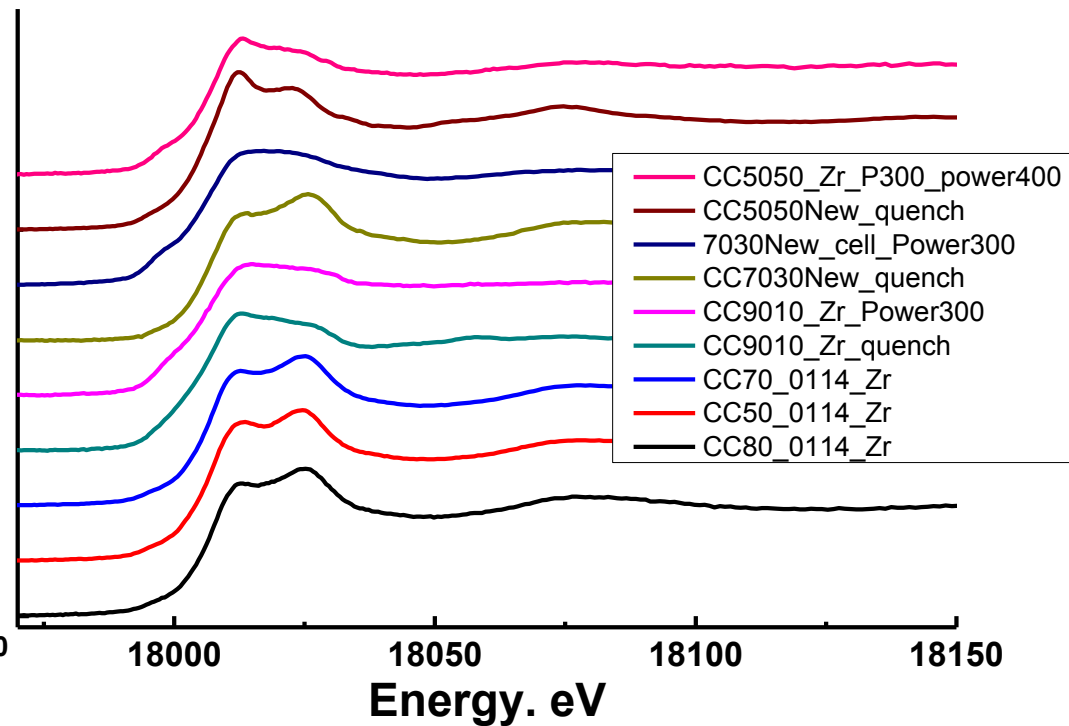
es (J.Pohlenz)

Zirconium XAFS

Quench

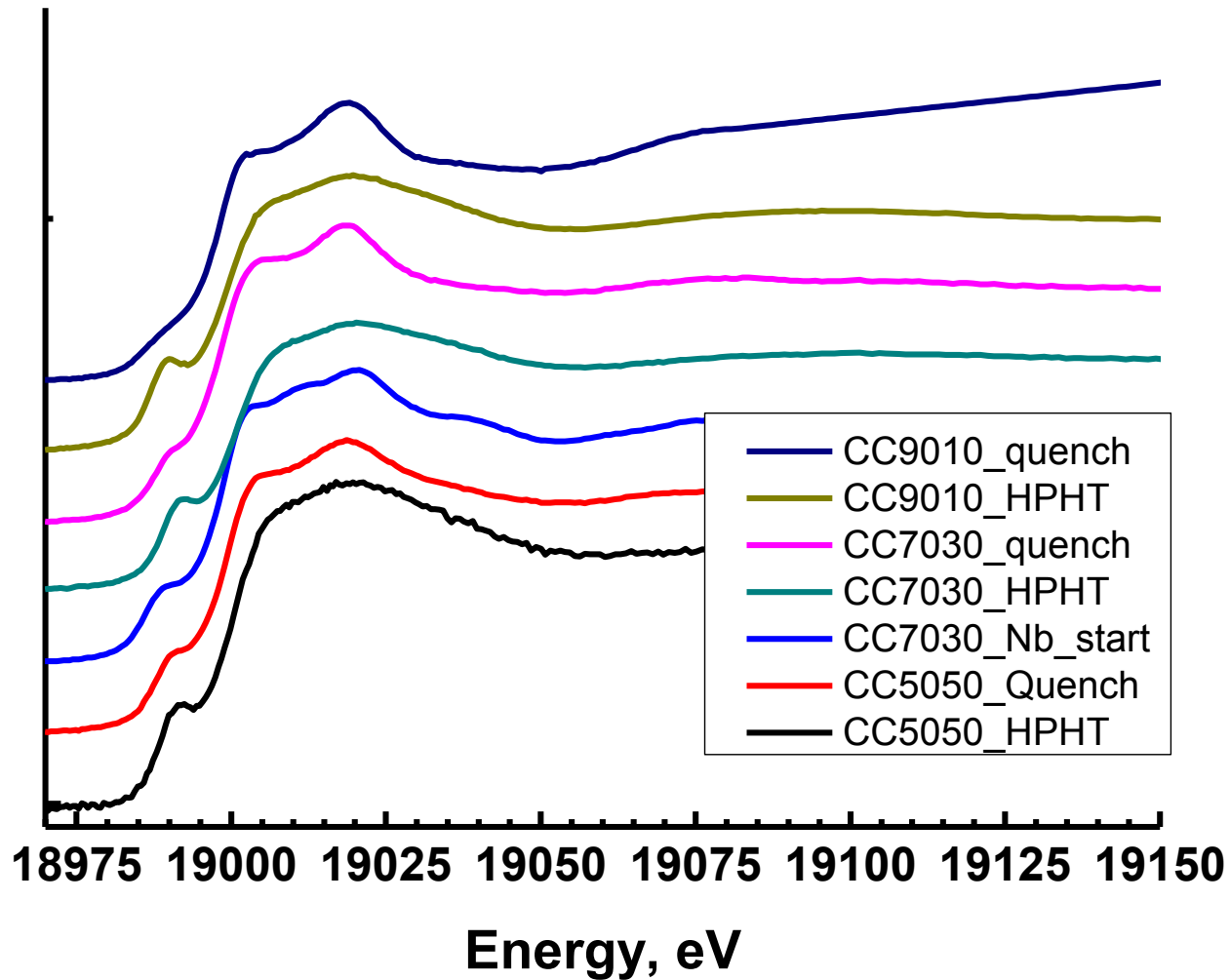


In situ at HPHT



Zr is largely dissolved in silicate glass and is likely 6-coordinated

Niobium XANES



Nb is not as Nb_2O_5 anymore, but is in pyrochlore-like environment

Conclusions

- Treatment of $\text{CaSiO}_3:\text{CaCO}_3$ system at 4-5.5 GPa – 1500-1700°C leads to formation of fine mixture of poorly crystalline nanosized carbonate, silicate glass and residual wollastonite.
- On micron-scale trace elements (Sr, Zr, Y) are homogeneously distributed.
- Strontium and yttrium partition between the silicate and carbonate phases; zirconium is largely retained in silicate glass.
- In the most carbonate-rich samples ($\text{CaSiO}_3:\text{CaCO}_3 = 50:50$) local environment of the studied elements differ considerably from more siliceous ones.