Using complementary microanalytical techniques to analyse diamond anvil cell experiments

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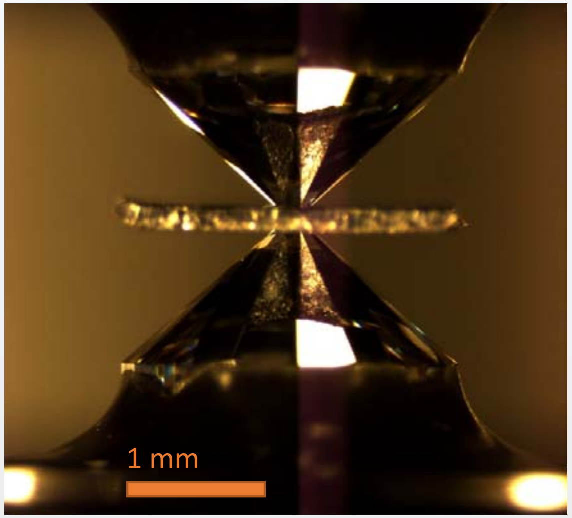
Outline

1. Introduction to diamond anvil cell (DAC) experiments
2. Analytical methods for DAC experiments
    1. In-situ analysis (within DAC)
    2. Preparing samples for ex-situ analysis
    3. Ex-situ analysis (recovered sample)
3. Combined approaches: Examples

Diamond Anvil Cell (DAC) Experiments



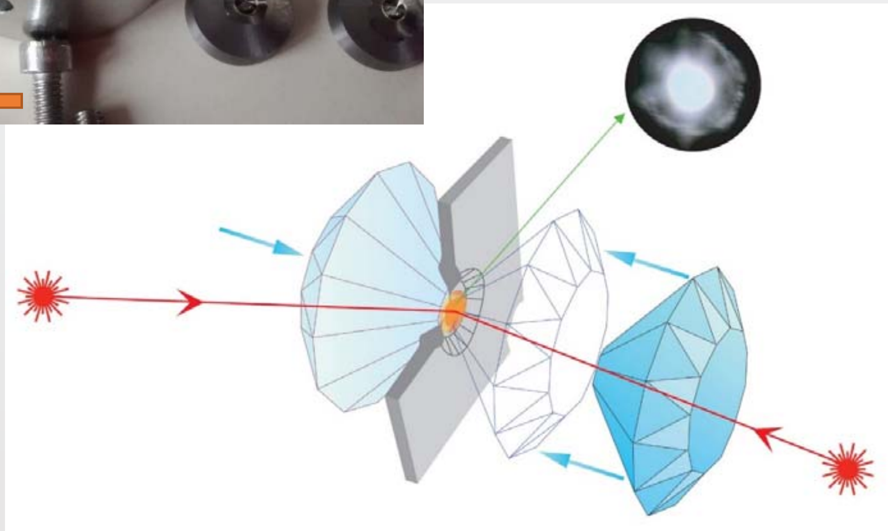
Aligned truncated diamonds with gasket

Some DACs

1 to > 120 GPa

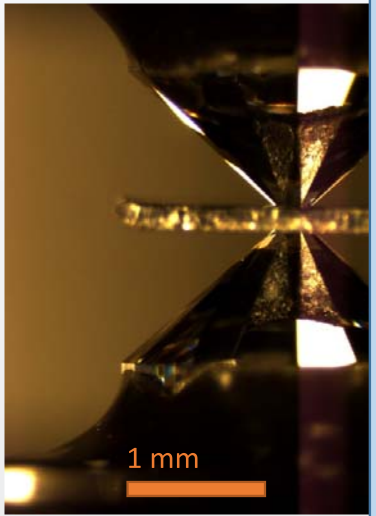
0 to > 5000 K

Laser beam path through diamonds



Laser Heating at Bristol Earth Sciences

Diamond Anvil Cell (DAC) Experiments

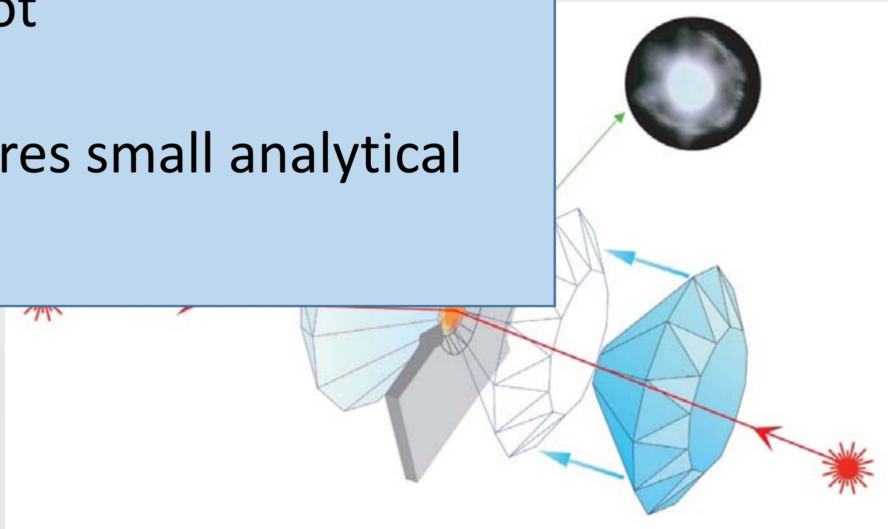


<ins>Analytical considerations</ins>

- Open diamond back = optical window, opportunity for in-situ analysis for diamond-penetrating methods
- Samples often altered or lost by quench or opening the cell: not all samples are recoverable (e.g. metallic H)
- When samples are recoverable, they are very small:
  - 10 micron diameter heated spot
  - Crystal sizes < 1 micron
  - Chemical inhomogeneity requires small analytical spot techniques

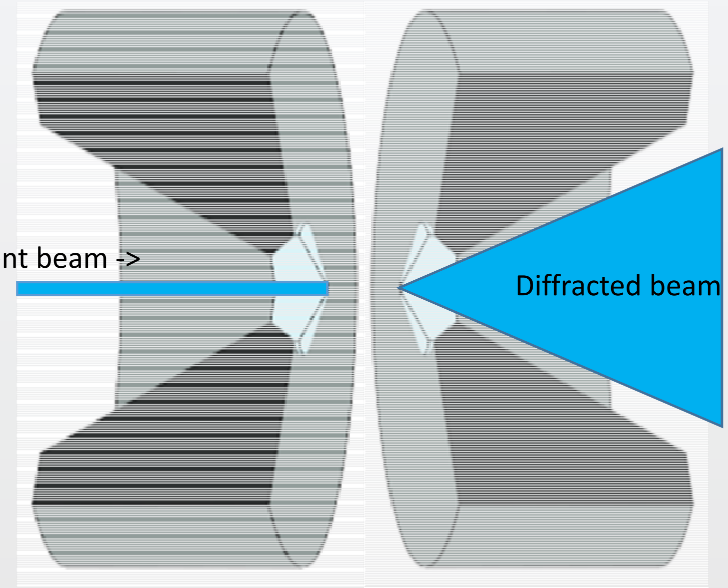
Laser Heating at Bristol
Earth Sciences

Laser beam path
through diamonds



In-Situ Diffraction Experiments (cold)

Cells have wide opening on backing plate



Incident beam ->

Diffracted beam -> detector

Adapted from Shen and Mao (2017) Rep. Prog. Phys 80

Low temperature: powder, single crystal

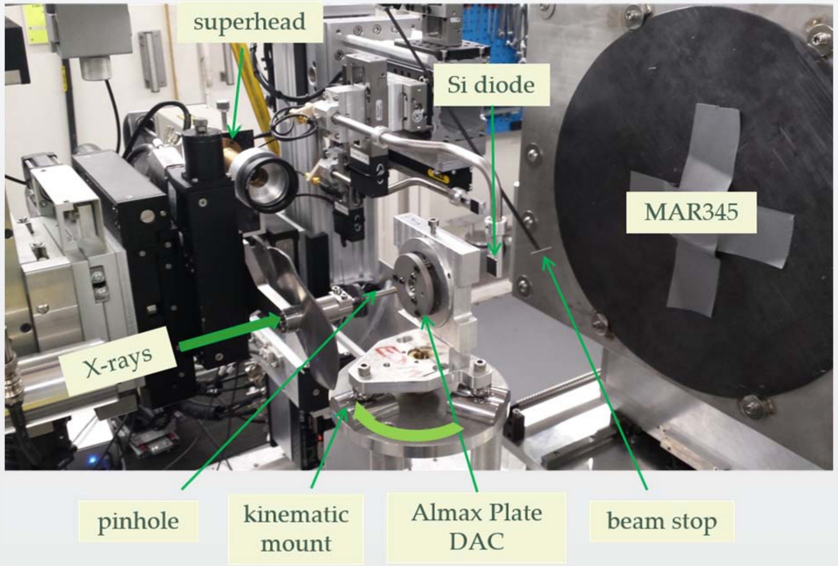
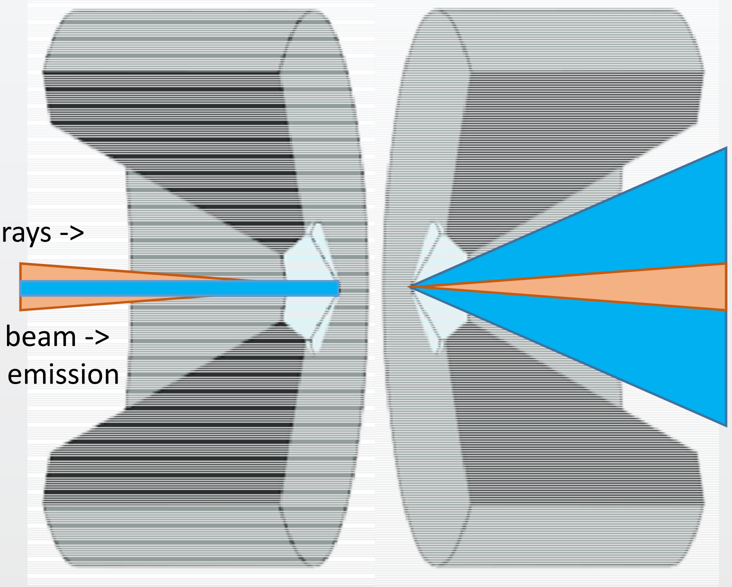


Image credit: Beamline I15, Diamond, UK

Also on ex-situ samples

Synchrotron X-ray source needed e.g. Diamond, UK

In-Situ Diffraction Experiments (hot)



Incident X-rays ->

Incident IR beam ->
<- Thermal emission

-> Diffracted X-rays

<- Incident IR beam
-> Thermal emission

Adapted from Shen and Mao (2017) Rep. Prog. Phys 80

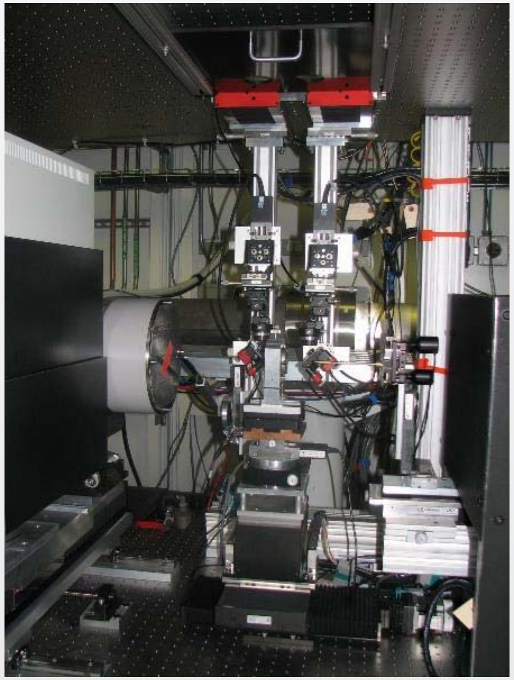
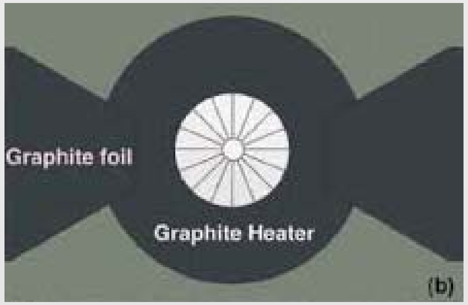


Image credit: HPCAT at APS

Double-sided laser heating: more difficult (laser optics, thermal emission measurement and X-ray beam paths…) e.g. HPCAT at APS

Or, resistive heating: more stable, more precise, no beam path problems, can use for single crystal, but far less high temperature and need TC in chamber

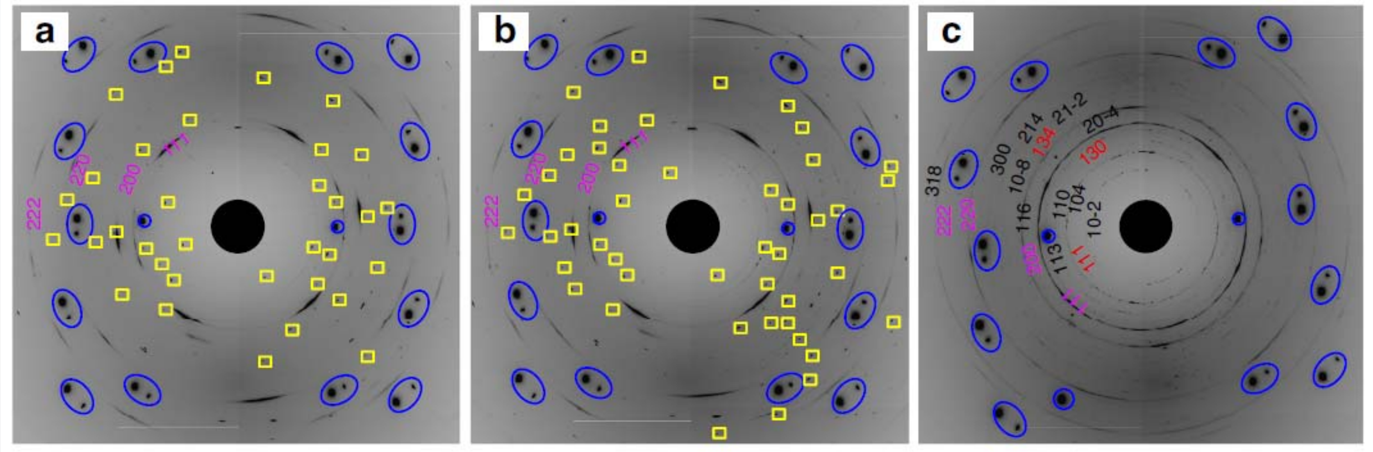
Du et al. (2013) Rev Sci Instrum



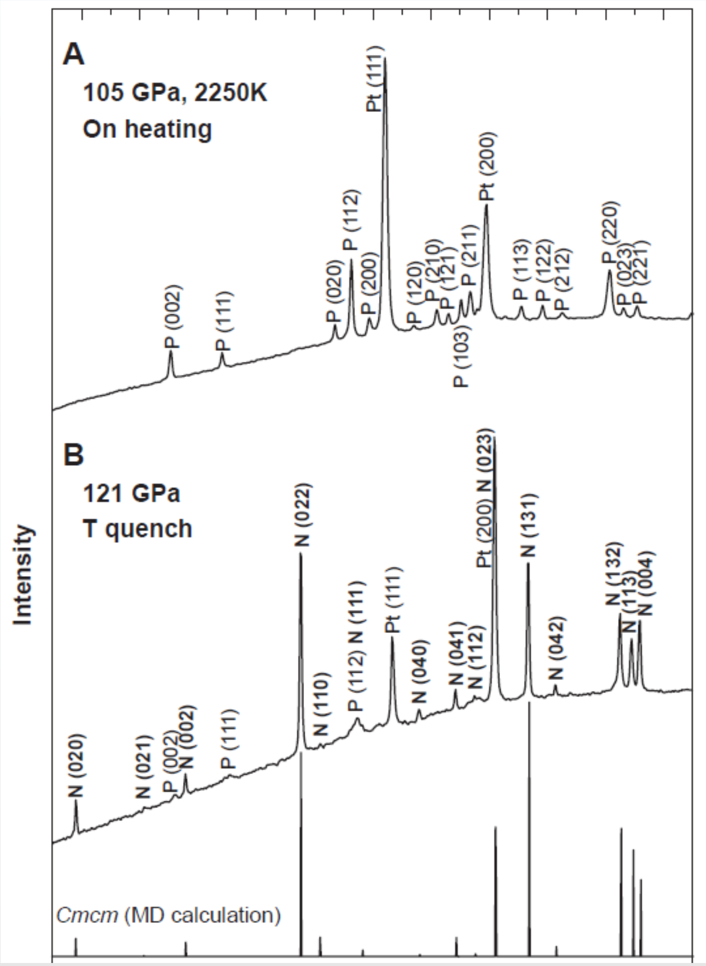
Synchrotron-source XRD

- Diffraction of X-rays through regular structure allows determination of structural data: phase identification, unit cell parameters
- In-situ (at high pressure +/- at high temperature)
- Ex-situ (measurement of cold product removed from DAC following pressurisation and laser heating)
- Powder or single crystal
- Examples in DAC:
  - [in-situ] compression behaviour, material equation of state, unit cell refinement, new material synthesis and characterisation, density of amorphous material (diffuse scattering)
  - [in- and ex-situ] phase relations e.g. the mineralogy of deep planetary interiors

XRD examples



[low-T]: single-crystal FeCO3, before (a) and after heating (b, c). Rings interpreted as melt & recrystallization. Cerantola et al. (2017), Nat. comm.

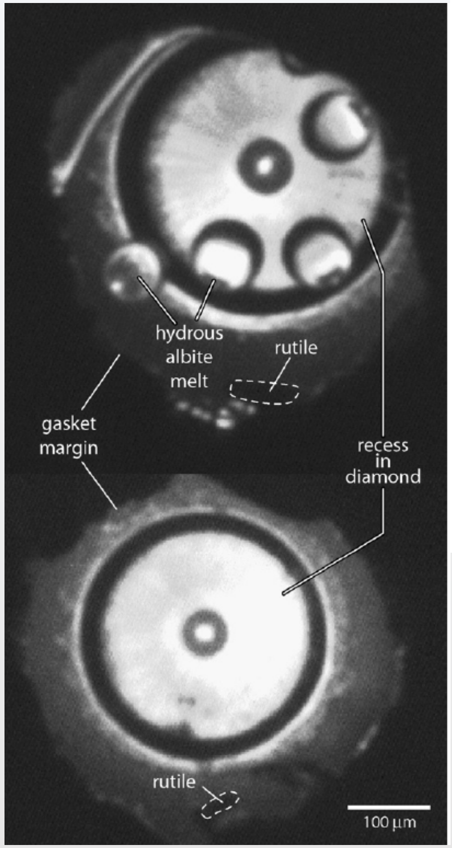


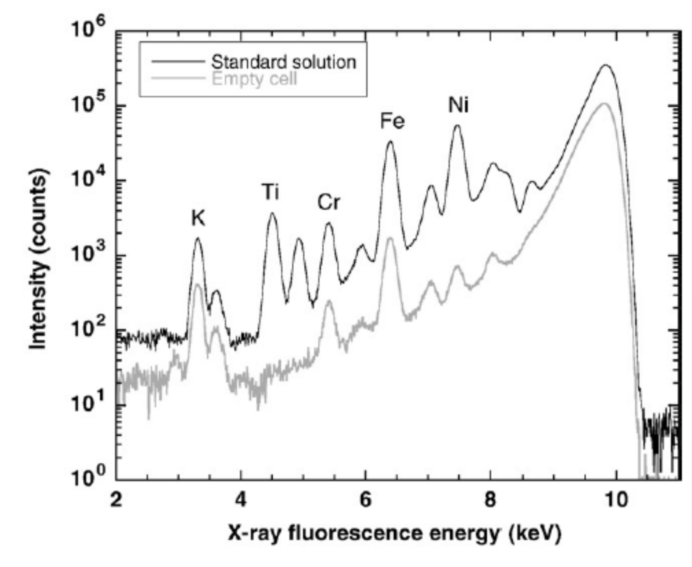
Discovery of post-perovskite. Murakami et al. (2004), Science. Measured at SPring-8

Synchrotron-source µXRF

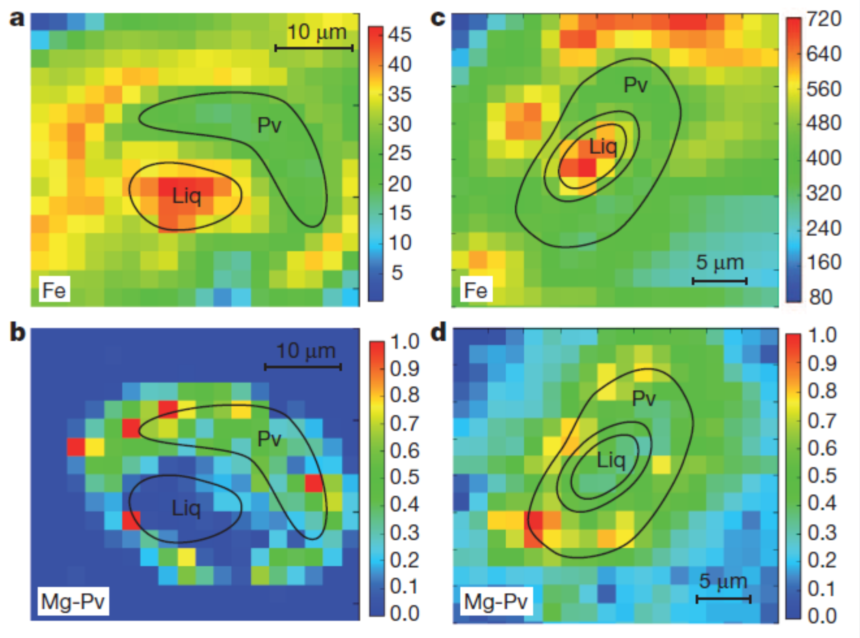
- Fluorescence of characteristic X-rays induced by primary X-ray beam: measured to determine composition
- Resolution may be limited by X-ray energy and secondary effects (enhancement) and matrix corrections needed
- Can be used on fluids as well as solids
- Examples in DAC: in-situ mineral solubility in hydrothermal DAC, phase compositions including co-existing liquid(s).

µXRF use: Examples



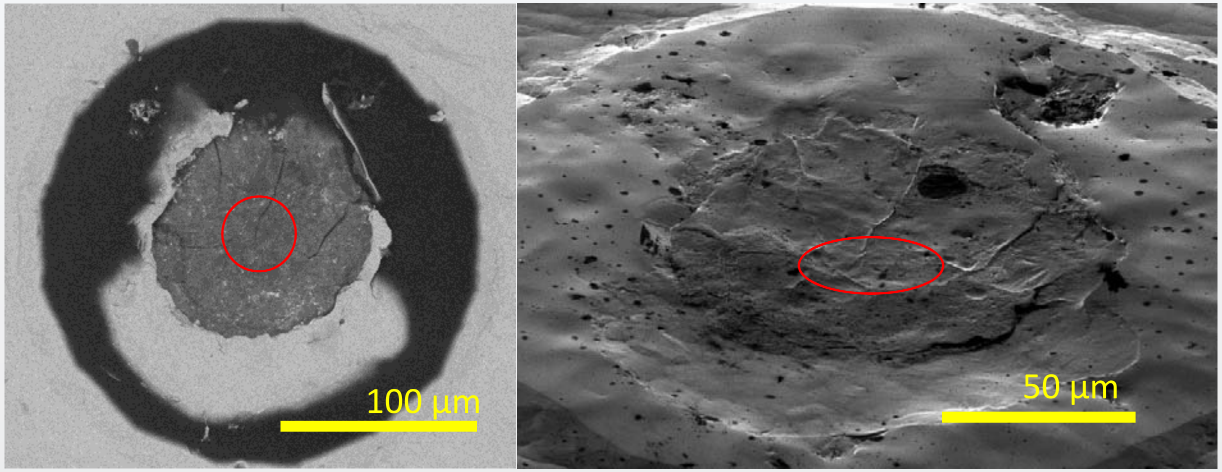


[in-situ] 1 GPa ~700 °C rutile solubility in hydrothermal DAC (Manning et al., 2008, EPSL).

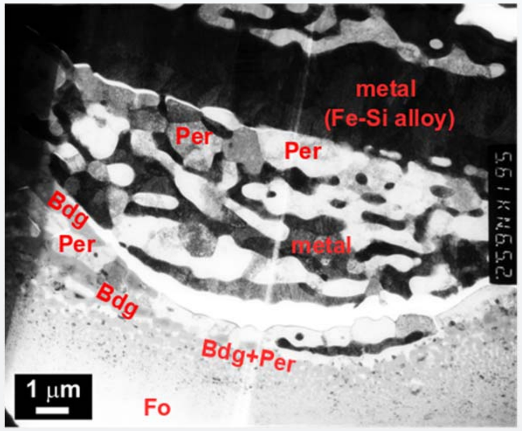


[ex-situ, quenched]: Silicate melting @ 58 and 113 GPa: Andrault et al. (2012), Nature. Phase identification by XRD.

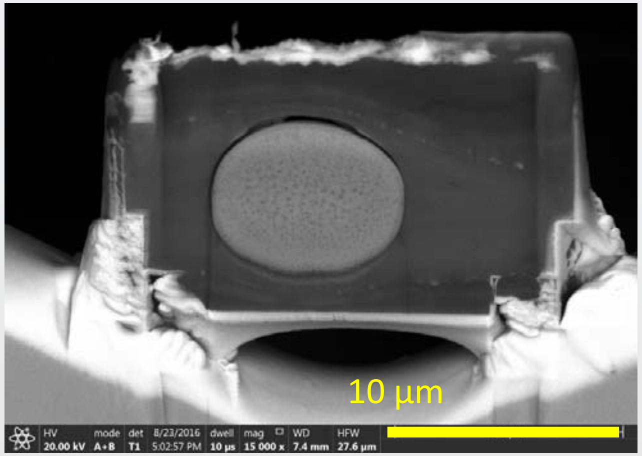
Heated experimental products



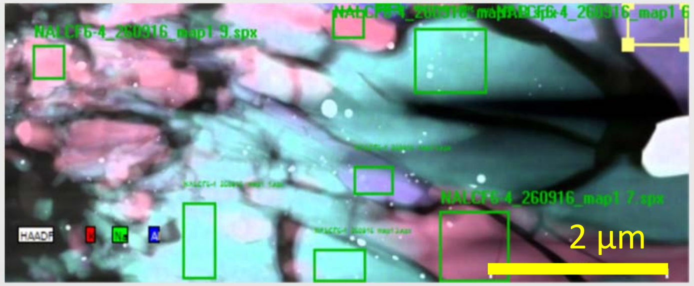
Subsolidus experiment: phase relations in K and Al-bearing silicate



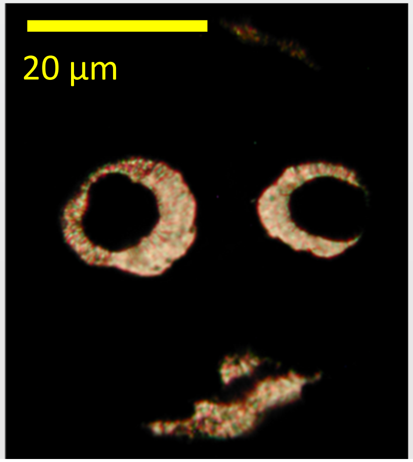
Fe metal heated with forsterite



Metal-silicate partitioning (supersolidus)



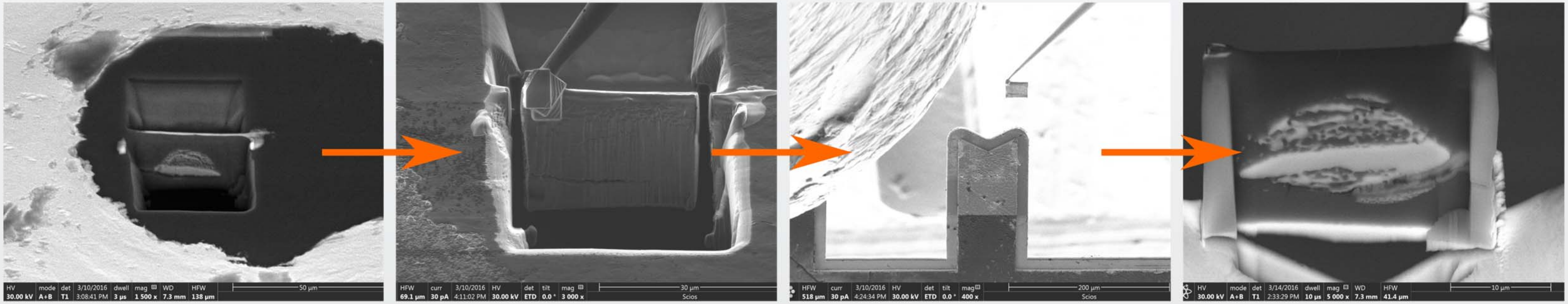
STEM image: crystalline phases



Transmitted light: Metal foil with
glass halos at heated spots

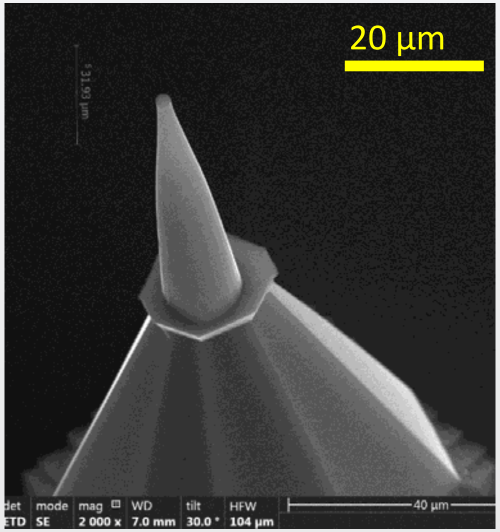
FIB sample prep for ex-situ measurements
1) Lamellae

Dual-beam Focussed Ion Beam: Ga^+ cutting & e^- imaging; deposition/welding and micromanipulation

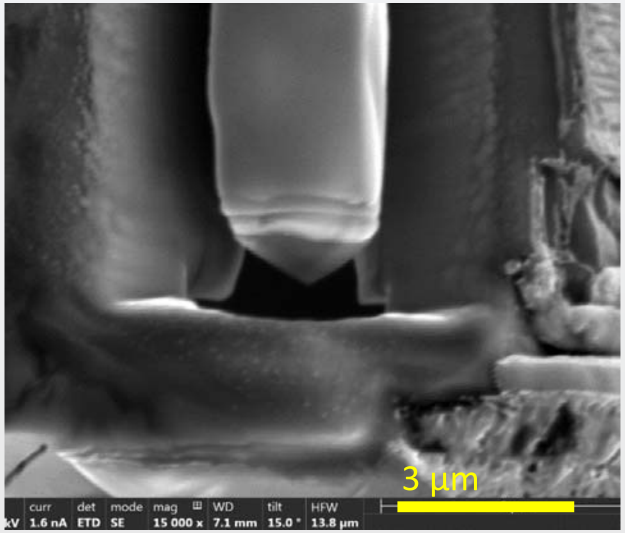


Preparing sample as a lamella for SEM, EPMA or TEM analysis by FIB. “Thick” SEM lamellae can be thinned for TEM analysis.

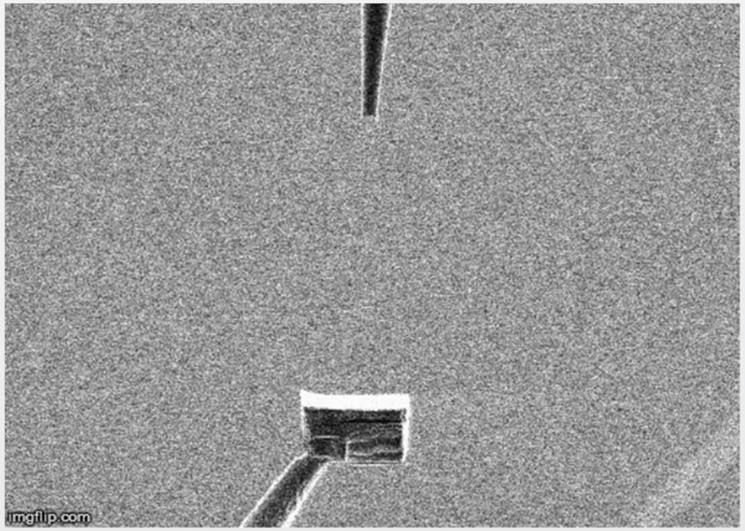
FIB sample prep for ex-situ measurements
2) Needle: Atom probe tomography



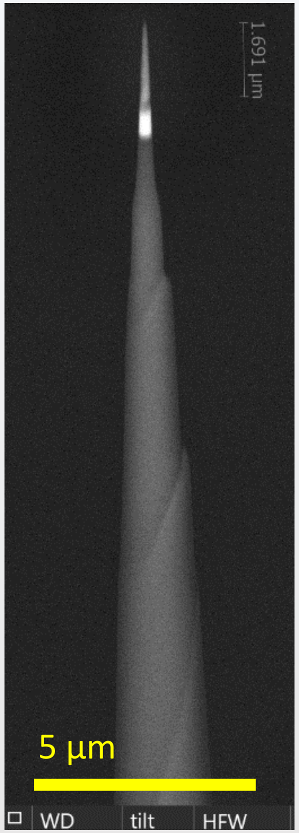
Si sample post



Wedge extraction



Welding

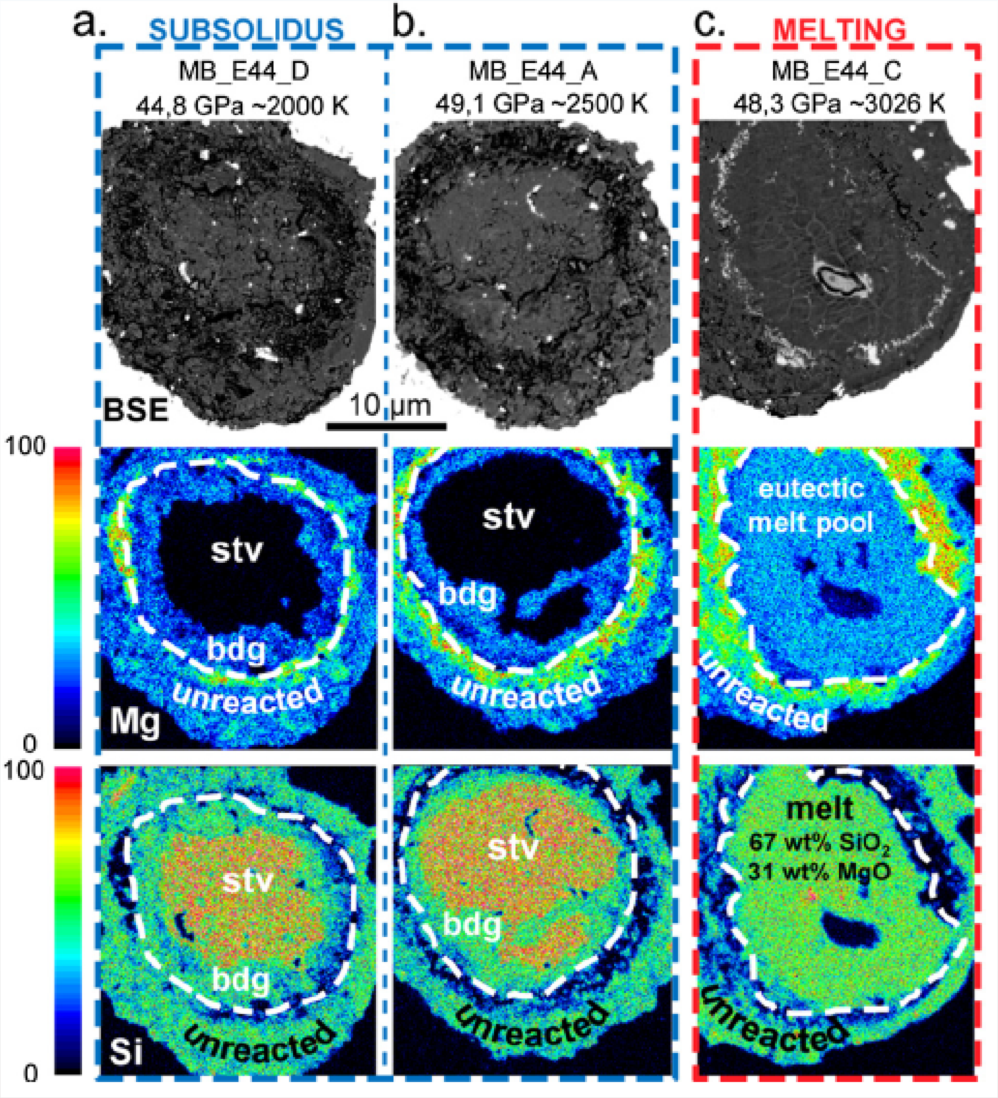


Annular milling for needle shaping and sharpening

Ex-situ analysis: Electron beam

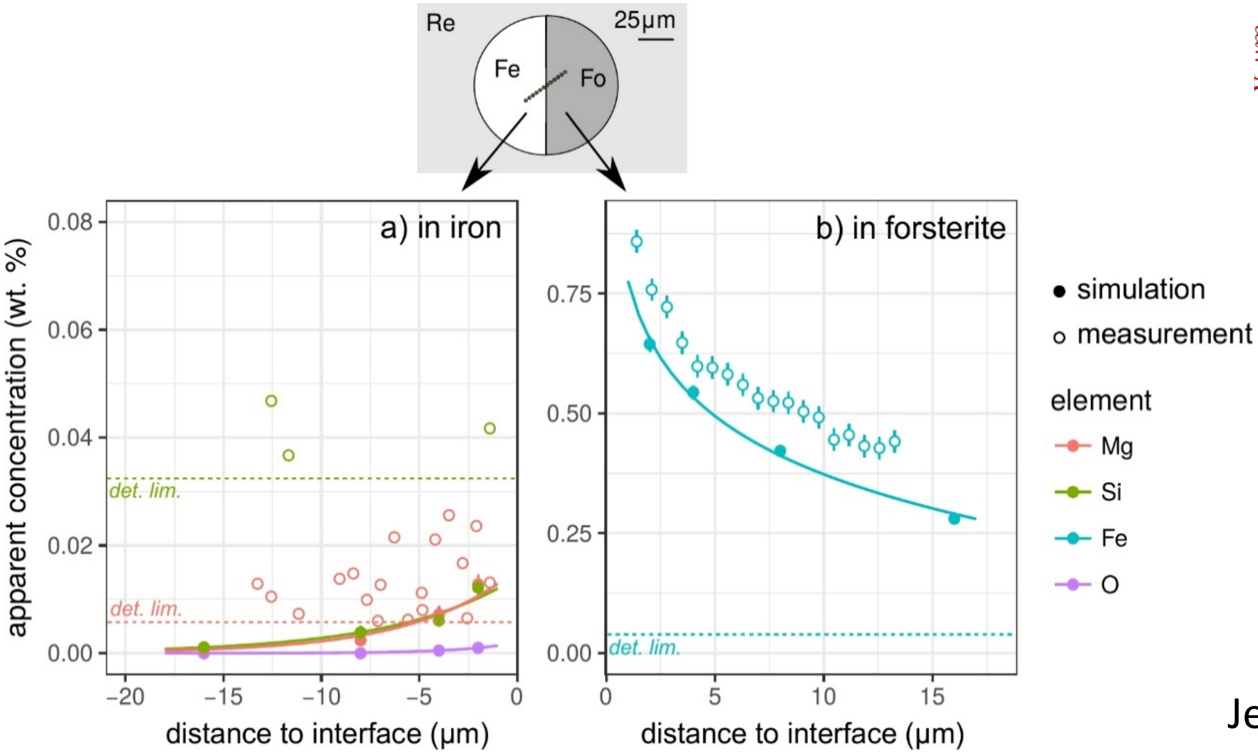
- EPMA, FE-EPMA (WDS / EDS)
  - Specific difficulties for small samples (i.e. DAC samples): fluorescence and thickness difficulties (Jennings et al. 2019 Microscopy&Microanalysis)
  - Low kV can be especially useful given intricate small-scale textures
  - Crystals usually < 1 µm
- SEM, FE-SEM
  - But usually not EBSD due to small crystal size
- TEM
  - STEM, EDS, EELS, electron diffraction
  - Thin samples, need site-specific preparation
- Examples in DAC: Phase composition and identity; compositional distribution (e.g. partitioning, diffusion) e.t.c.

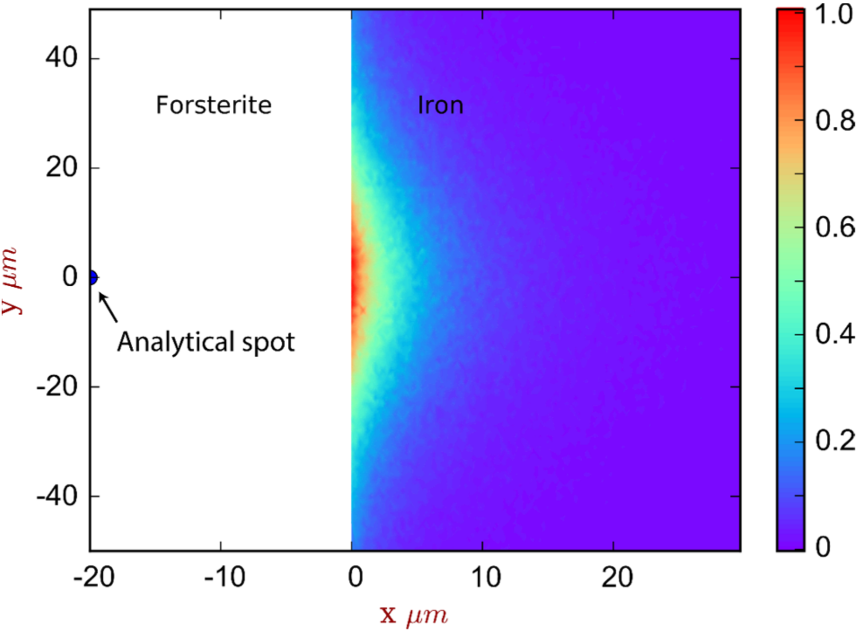
Example



Phase relations in MgO-SiO2 at lower mantle conditions
Baron et al. (2017) EPSL
FE-EPMA, 5 keV

EPMA and SEM small sample limitation: fluorescence



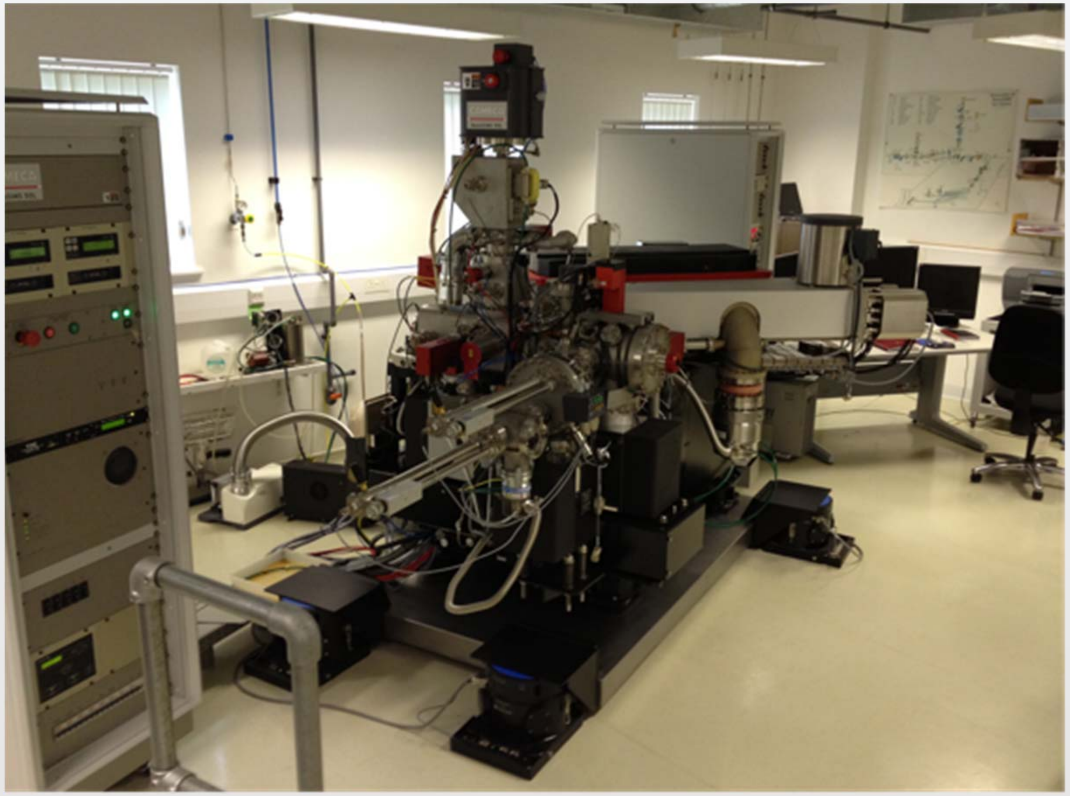


Jennings et al. (2019) M&M

Ex-situ analysis: nanoSIMS

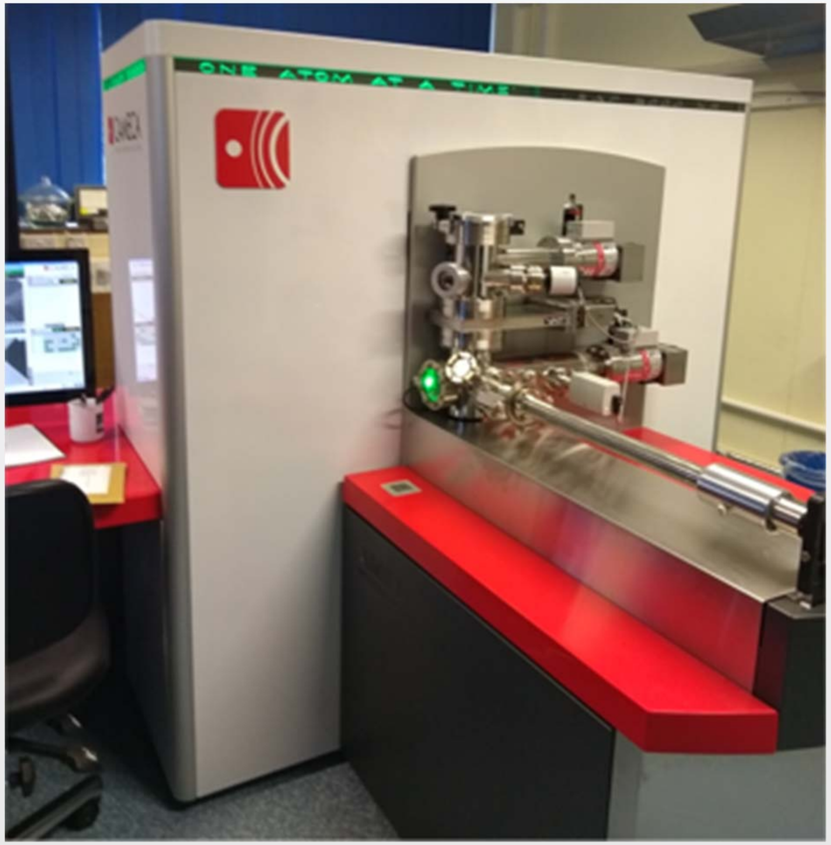
- Primary ion beam (O^- or Cs^+) ion
- Play-off between resolution and sensitivity; down to < 100 nm
- Isotopic detection and mapping
- Matrix-dependent. Effect of tricky sample geometries?
- Examples in DAC: Composition distribution studies e.g. partitioning, diffusion, inc. isotopic

Cameca nanoSIMS 50L, Open University



Ex-situ analysis: APT

- Atomic identification and 3D position i.e. nano-scale 3D mapping
- Isotopic identification
- Powerful technique. Geometry and chemical quantification dependant on processing. Difficult sample preparation; expensive. More difficult on non-conductive and mixed material samples
- Examples in DAC: little-used technique for DAC experiments but much potential: composition distribution, defect decoration, diffusion and distribution, complex materials e.g. layered



Atom probe, Oxford University

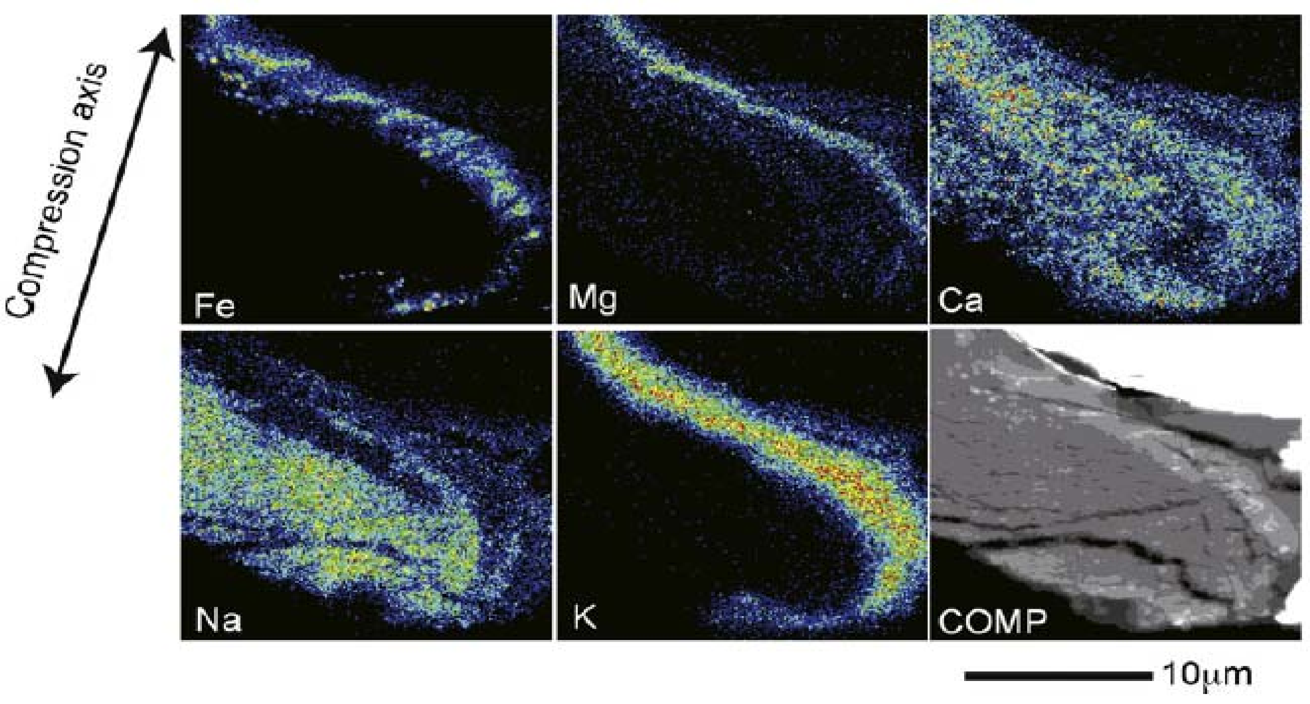
Complementary techniques for DAC experiments

- Can be powerful to follow in-situ XRD phase determinations with compositional measurements, for example.
- Ex-situ analysis can corroborate in-situ measurements, find problems and assist interpretation
- Different scales of measurement

Some Earth science case studies:

1. Chemistry and mineralogy of Earth’s lowermost mantle
2. Melting and crystallisation in a deep magma ocean
3. Linking subducted oceanic crust to ultradeep diamonds
4. Metal-silicate partitioning experiments for planetary core formation

Soret diffusion in the DAC: importance of complementary techniques

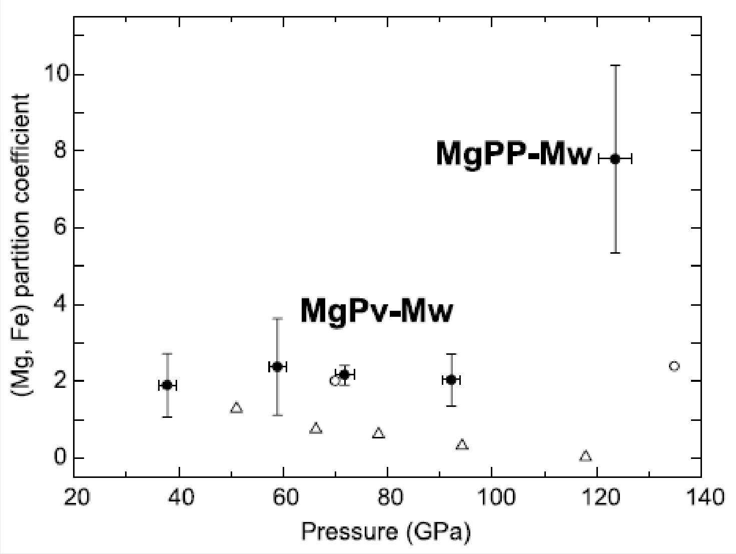


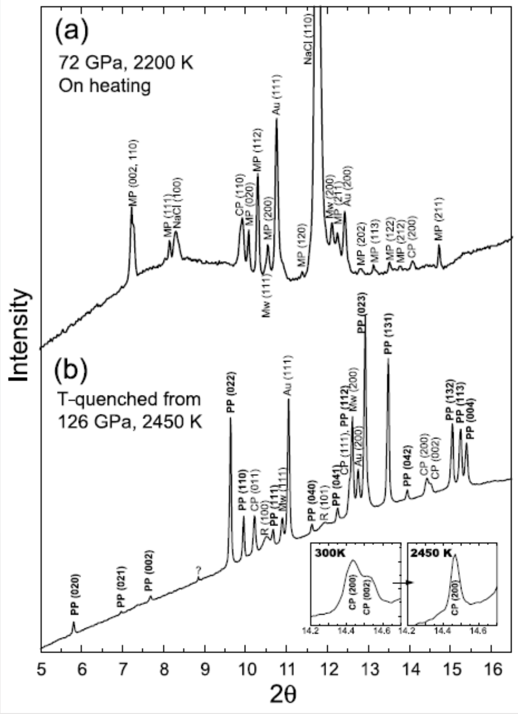
Redistribution of components around heated spot in granitic glass.
Sinmyo and Hirose (2010, PEPI)

1) Chemistry and mineralogy of Earth's lowermost mantle

- Bridgmanite transition to post-perovskite at 113 GPa (XRD of DAC, Murakami et al., 2004, 2005)
- Mg/Fe ratio in bridgmanite relative to periclase: XRD vs TEM
    -> implication: viscosity, heat flow, electrical conductivity, melting T

$$\frac{\left(\frac{\mathrm{Fe}}{\mathrm{Mg}}\right)\mathrm{MW}}{\left(\frac{\mathrm{Fe}}{\mathrm{Mg}}\right)\mathrm{Pv}}$$

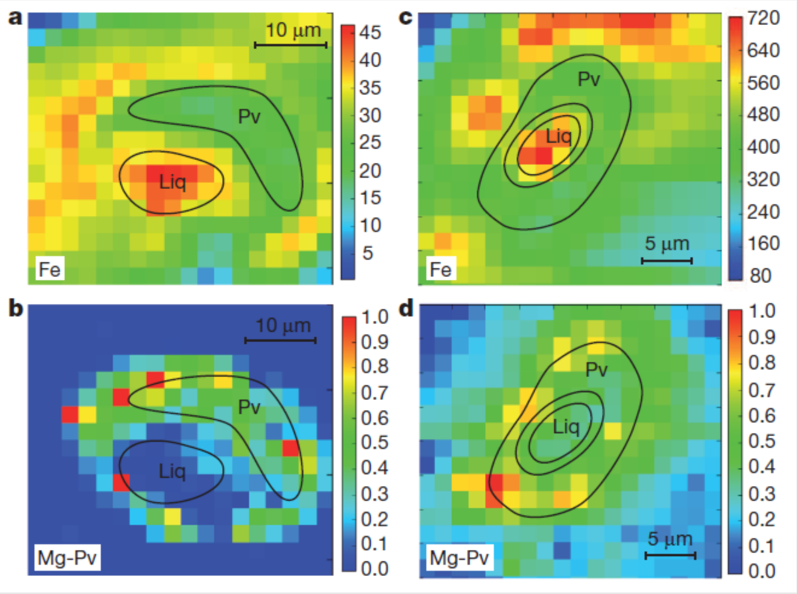




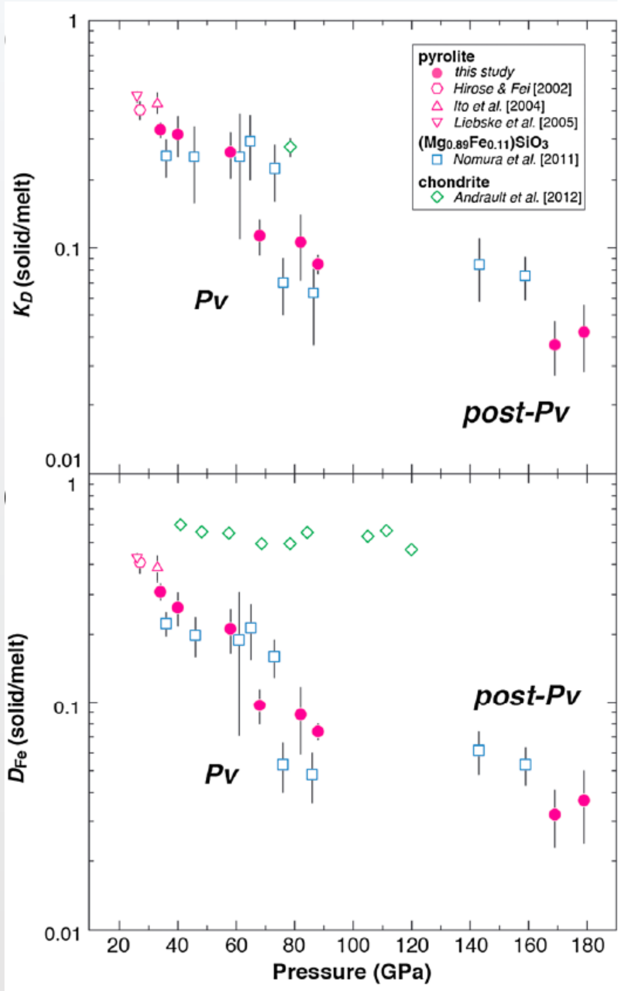
Murakami et al. (2005) GRL

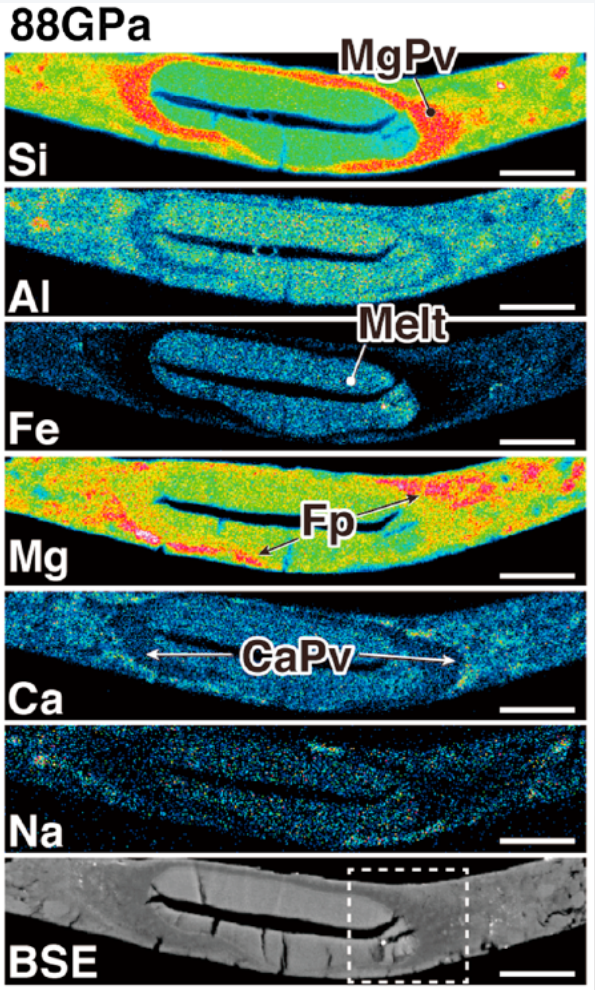
2) Melting and crystallisation in a deep magma ocean

XRF vs. FE-EPMA for lower mantle mineral-melt partitioning



XRF: Andrault et al. (2012), Nature: liquid less Fe-rich; buoyant.

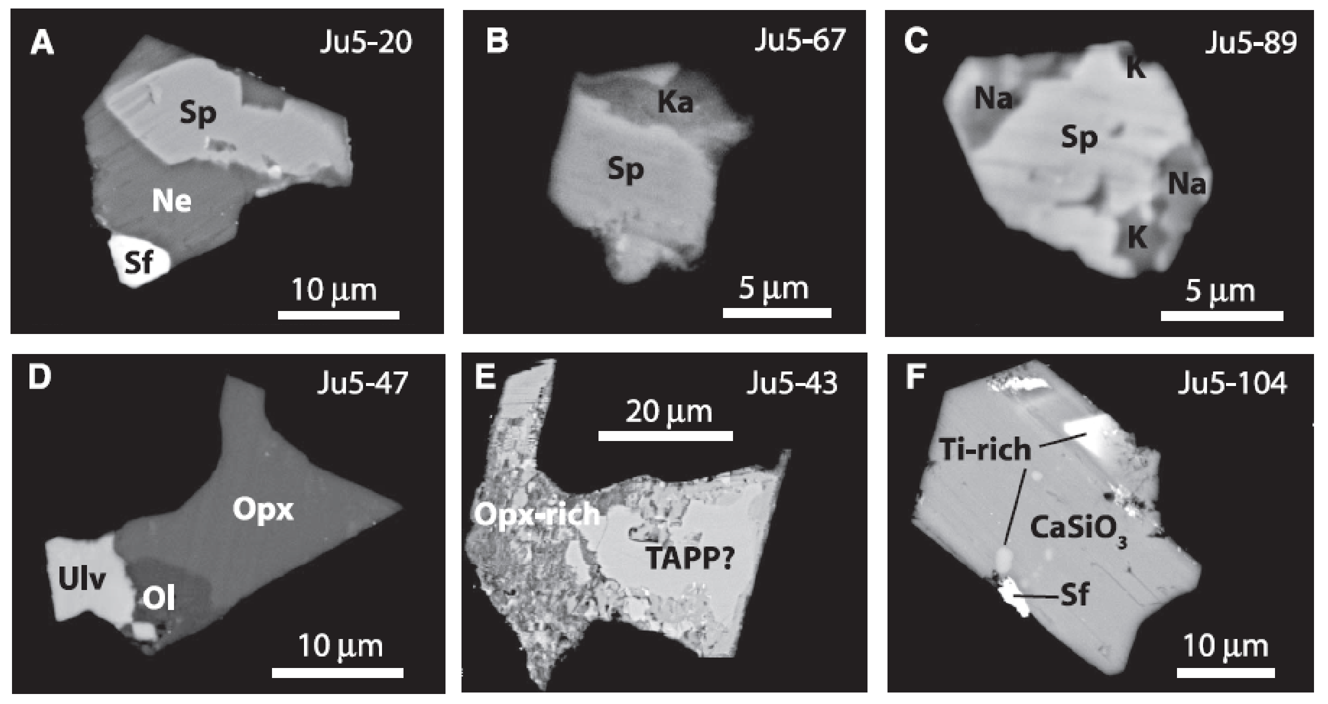




FE-EPMA: Tateno et al. (2014), JGR: Solid Earth

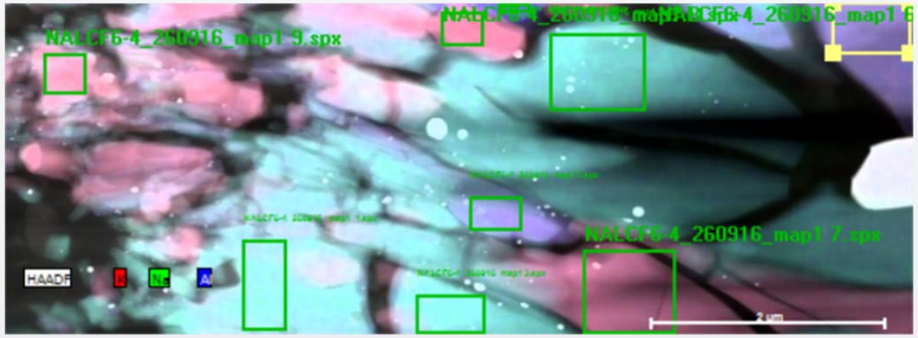
3) Linking subducted oceanic crust to ultradeep diamonds


Springer



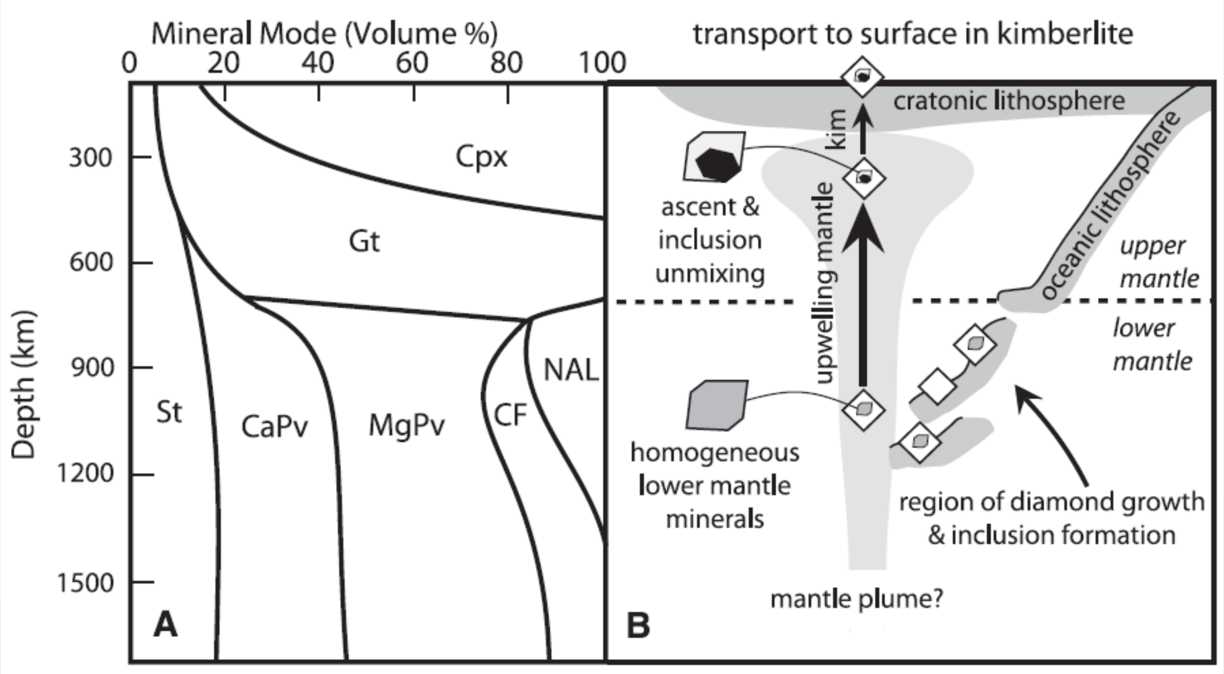
Walter et al. (2011), Science
I. Buisman

3) Linking subducted oceanic crust to ultradeep diamonds



Phase relations in the K- and Na- bearing aluminous silicates, to study NAL and CF phase stability. Interpretation through:

- XRD
- EPMA
- TEM

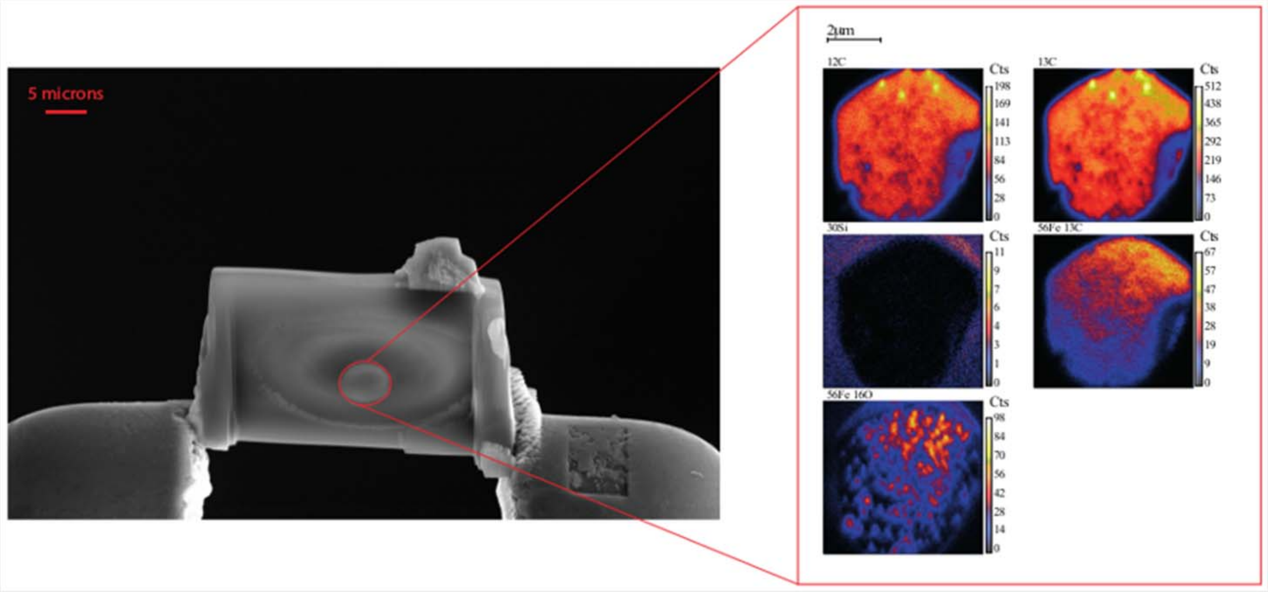


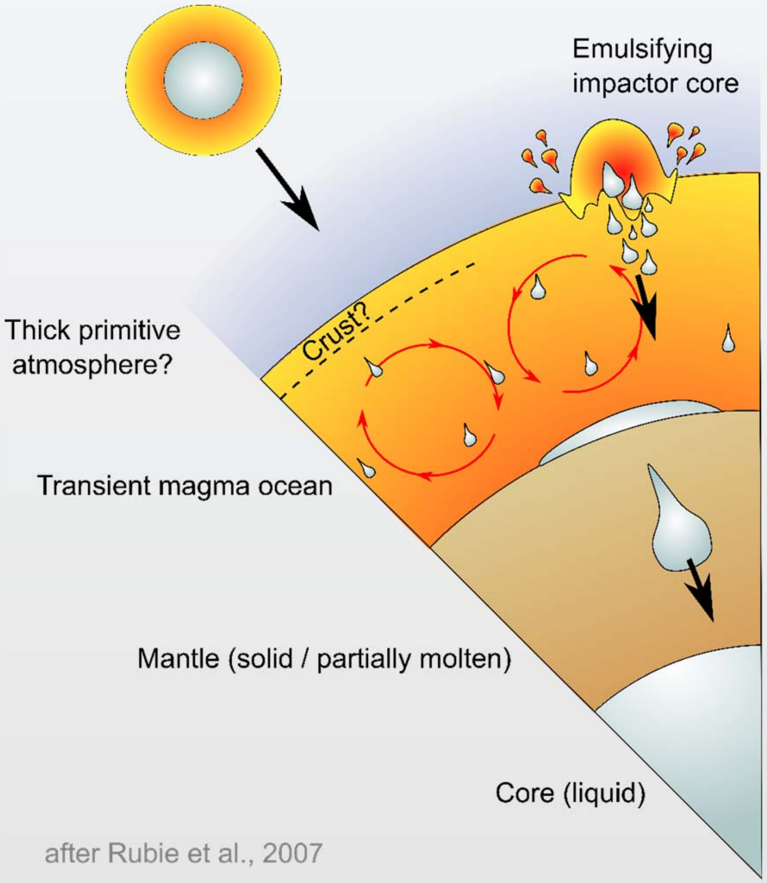
Walter et al. (2011), Science

4) Metal-silicate partitioning experiments for planetary core formation. A) Carbon

Carbon partitioning: silicate-metal super-liquidus experiments to 80 GPa

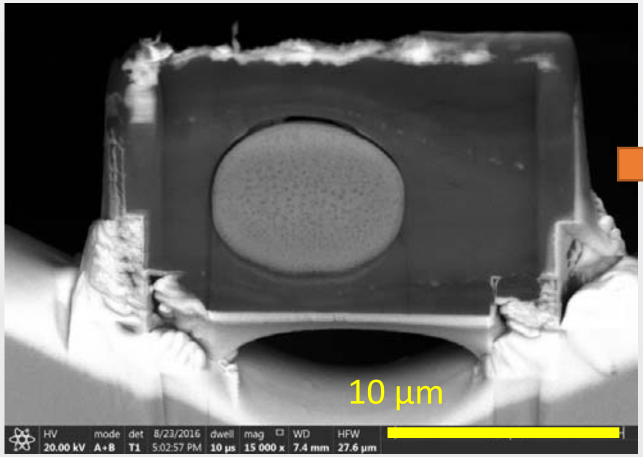
- Metal: EPMA (1-3 wt.%)
- Silicate: nanoSIMS (50-500 ppm)





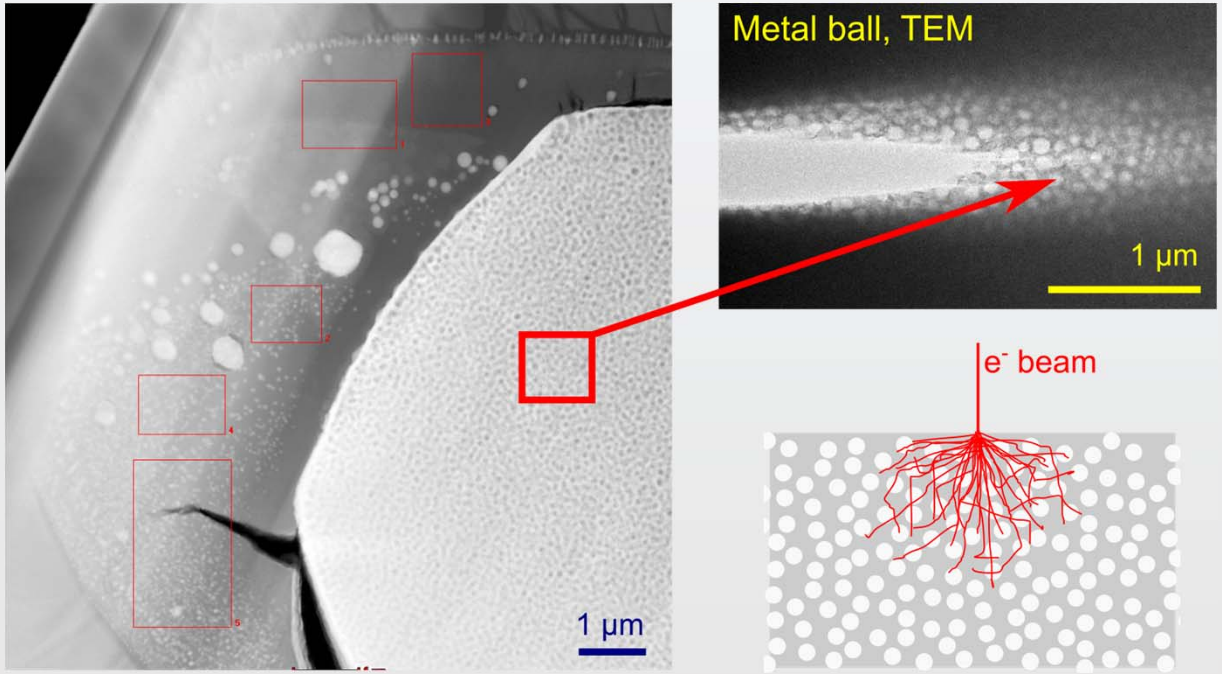
after Rubie et al., 2007

4) Metal-silicate partitioning experiments for planetary core formation. B) micro/nano textures



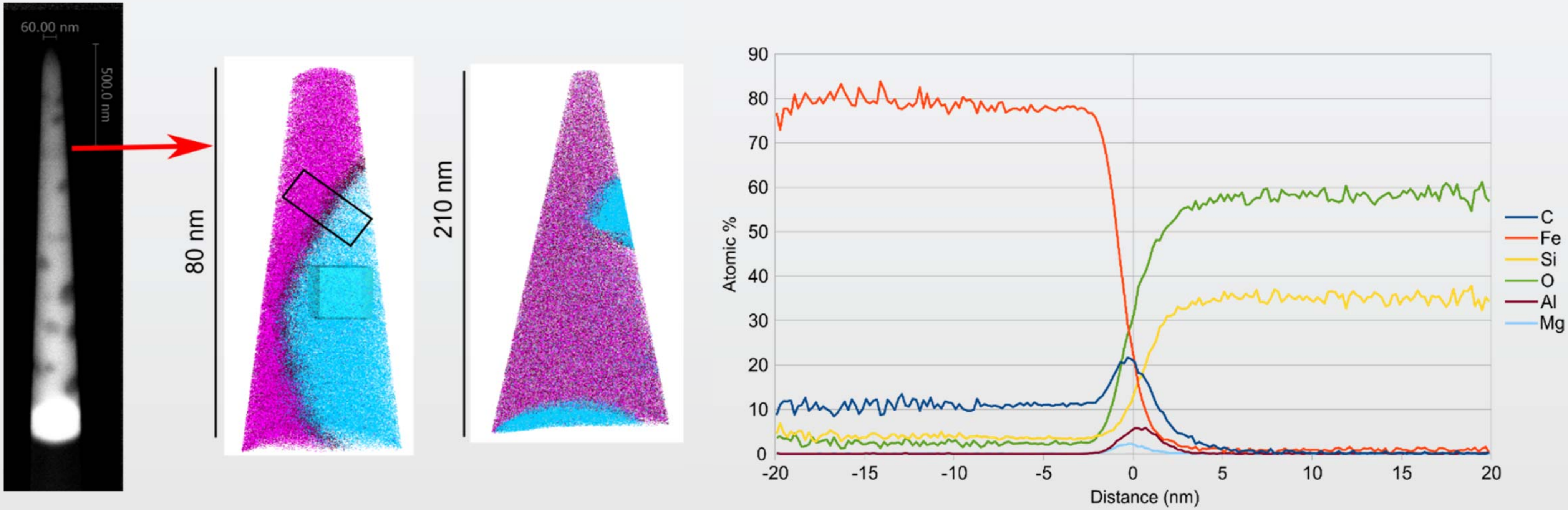
Metal-silicate partitioning (supersolidus)

TEM bright-field



STEM, HAADF

4) Metal-silicate partitioning experiments for planetary core formation. B) micro/nano textures



Summary

- DAC experiments allow various materials to be held at the static pressures found deep in planetary interiors
- Experimental samples analysed either in the DAC (during or after heating) or removed from DAC
- In-situ: Synchrotron techniques e.g. XRD, XRF
- Ex-situ: E-beam (EPMA, TEM, SEM); nano-SIMS; APT
- Complementary techniques powerful:
  - Combine structure and chemistry
  - Ground-truth in-situ measurements with follow-up microbeam
  - Diagnose interpretation problems e.g. chemical diffusion effect on phases
- Many uses in Earth and planetary sciences: planetary interiors