Do grain boundaries act as a water reservoir in Earth's mantle?

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Where is water stored in mantle materials on the grain scale?

- Recent models suggest there is 1-7x amount of water in Earth's mantle as in all Earth's oceans (Peslier *et al*., 2017)
  - Water lowers the viscosity of mantle rocks deforming by both dislocation creep and diffusion creep
  - Directly impacts Earth's geodynamic behaviour

- Grain boundaries proposed to have concentrations of water hundreds of times greater than grain interiors, because they are disordered environments compared to crystal lattices (e.g. Hiraga *et al*., 2007)
  - Chemical segregation at boundaries influences grain boundary diffusivity, which impacts bulk viscosity of diffusion creep (Marquardt and Faul, 2018)
  - Creep strength of water-rich olivine aggregates deforming by DisGBS is much lower than strength of water-rich olivine deforming by dislocation creep (Ohuchi *et al.*, 2015)

Where is water stored in mantle materials on the grain scale?

- Previous evidence for chemical partitioning at grain boundaries
  - EPMA – incompatible element partitioning at grain boundaries (Ca; Hiraga *et al.*, 2004)
  - Synchrotron FT-IR – H_2O-enriched regions close (tens µm) to boundaries (Sommer *et al.,* 2008)

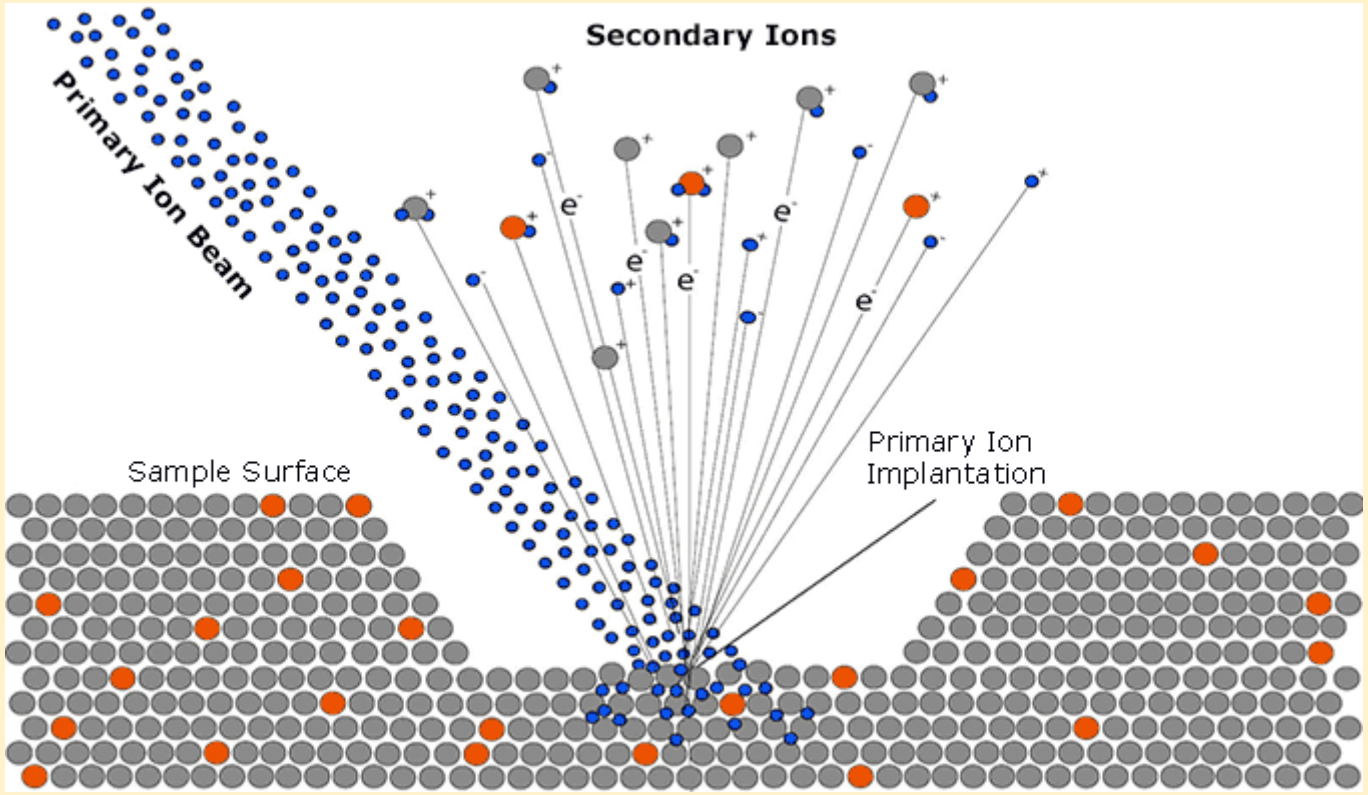
At mantle P-T conditions, H_2O dissociates to H^+ and OH^-

- But enrichment of water (H^+) itself has never been imaged at the scale of grain boundaries (~1 nm), because of the small scale of the target, and the experimental challenges of detecting H^+ by traditional analytical techniques
- Nanometer-scale resolution secondary ion mass spectrometry (NanoSIMS) may help to resolve this issue
  - Spatial resolution limit of 50 nm
  - Detection limits of ppm to ppb, depending on element

How Secondary Ion Mass Spectrometry works

A beam of primary ions (we used Cs^+) is used to sputter particles from the sample surface

Some of the liberated particles are ionised (i.e. secondary ions)

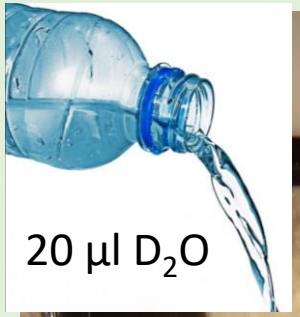


The secondary ions are directed to a mass spectrometer using magnets

Image source: www.cameca.com/products/sims/technique

To perform the NanoSIMS tests, we first made some synthetic mantle, doped with heavy water (D_2O)

^2H used as easier to detect than ^1H by NanoSIMS, and to distinguish from atmospheric water



Sealed capsule so D_2O could not escape during the experiment

Equivalent to a depth of ~10 km

Olivine (80 wt%) + enstatite (20 wt%) powder

Stainless steel

Fo100 bicrystal (not used in this study)

nickel

Fo89 single crystal (not used in this study)

Experimental conditions:

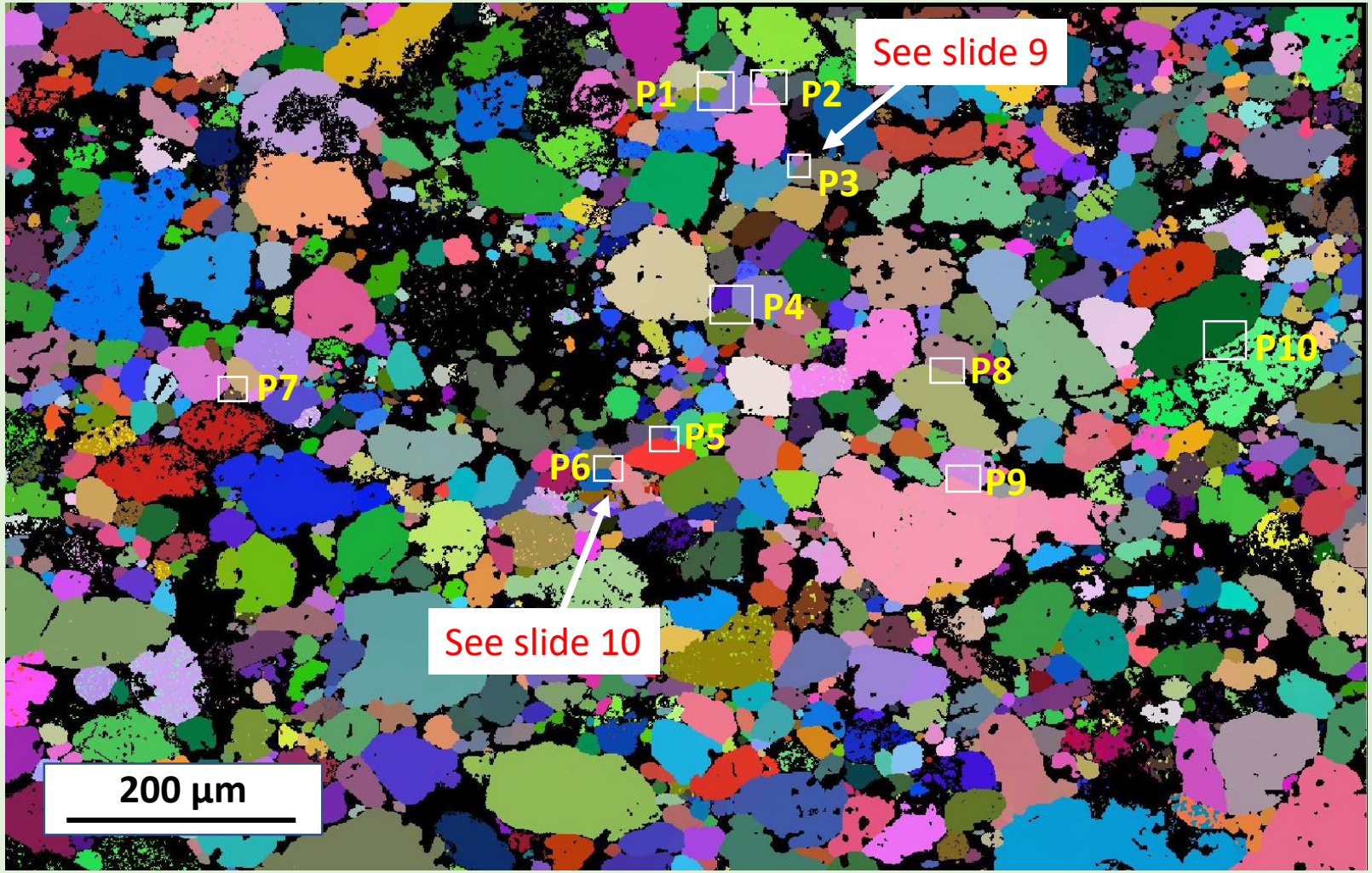
T = 1250 °C,

P = 0.3 GPa,

t = 3 hours

long enough for equilibrium concentration of H to be attained in grain interiors via lattice diffusion

We collected EBSD before NanoSIMS



because NanoSIMS signal at grain boundaries can depend on:

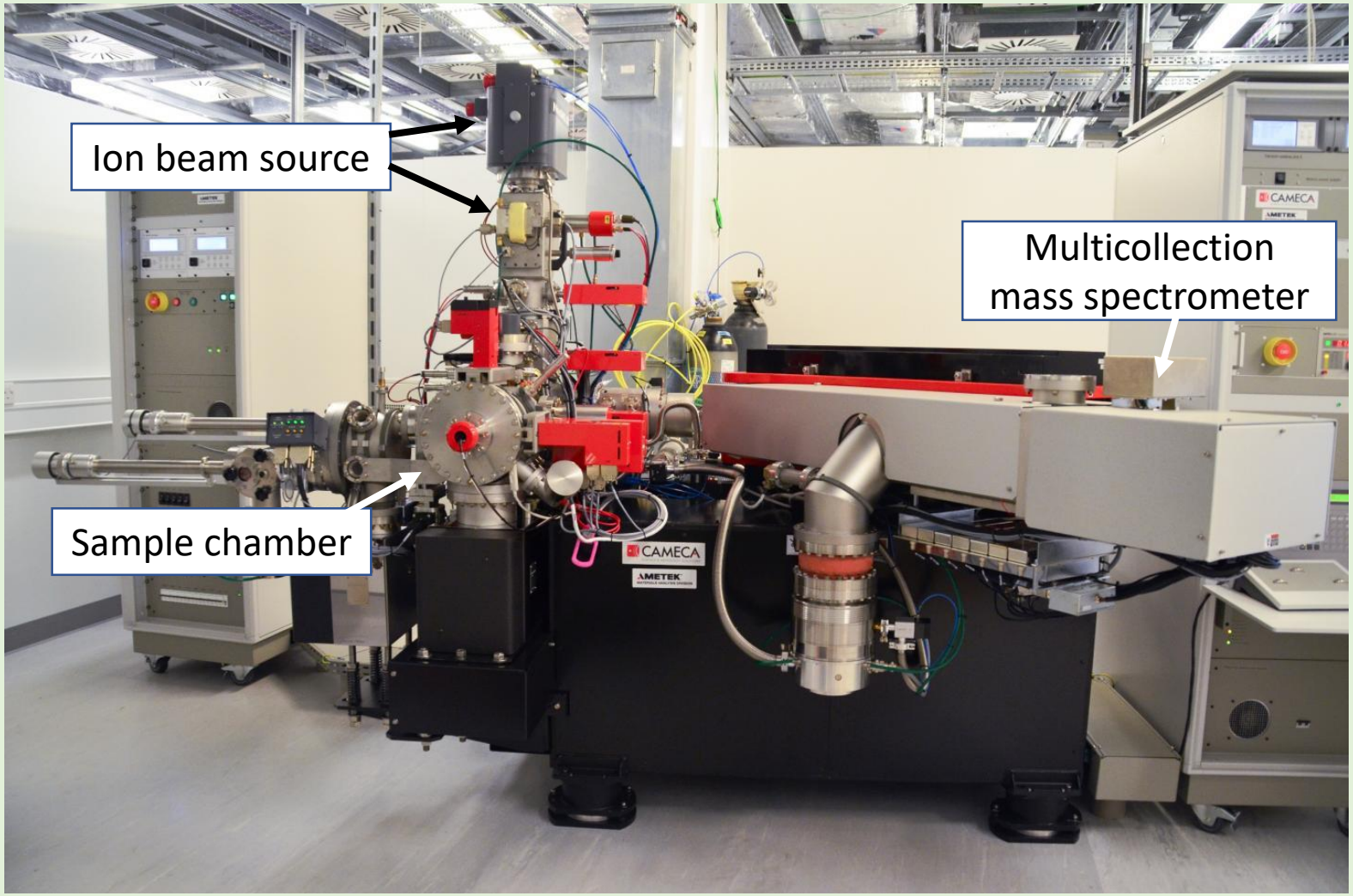
- Orientation of lattice with respect to beam
- Angle of boundary with respect to beam
- Misorientation between grains

White boxes indicate NanoSIMS sites

- Data were collected at triple junctions to acquire information from three boundaries per site
- Not all sites of interest yielded clear results

We collected NanoSIMS data on the Cameca NanoSIMS 50L at the University of Manchester

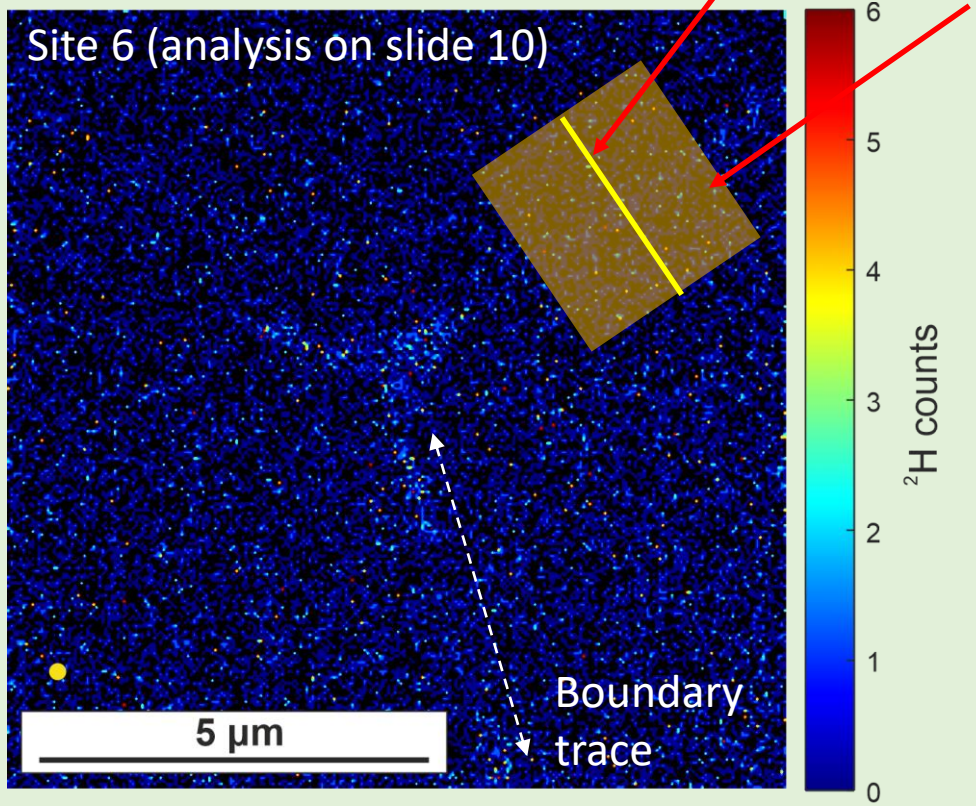
Photo credit:
K Moore, Manchester



^{2}H maps from NanoSIMS

The ^{2}H map data are summed from 1000 frames

Yellow dot indicates spot size of beam during scan (200 nm diameter)



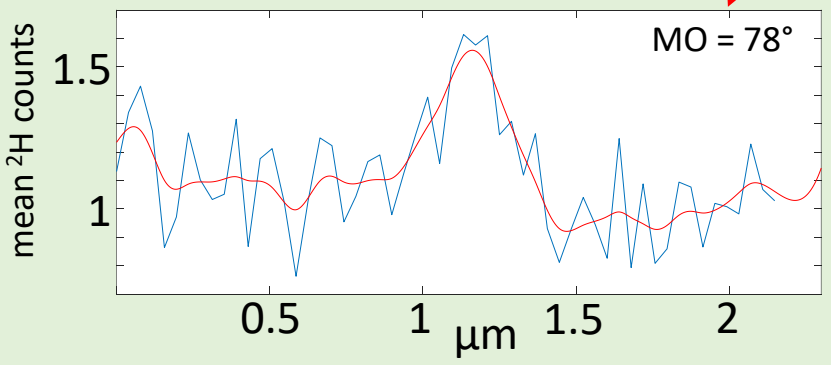
Actual line drawn

Area that the boundary profiles are constructed from

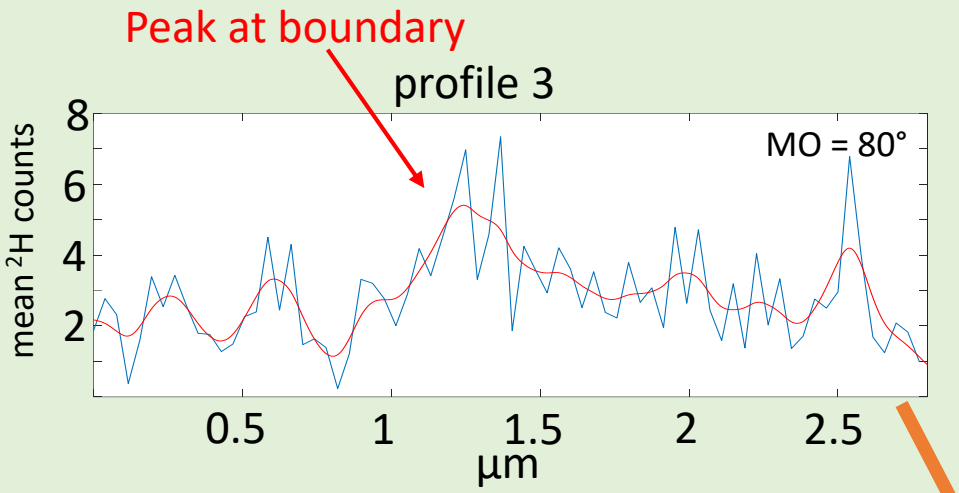
Boundary profiles are drawn perpendicular to boundary, as judged by eye

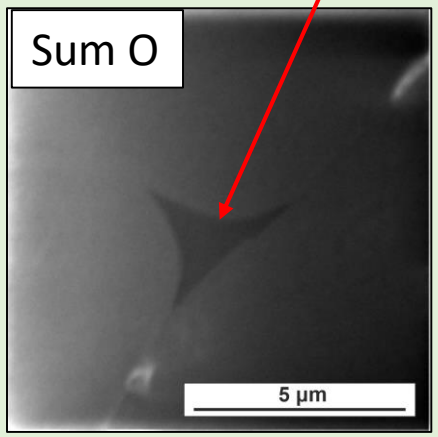
Counts are averaged over a line width that incorporates multiple (50 or 100) pixels along the length of the boundary

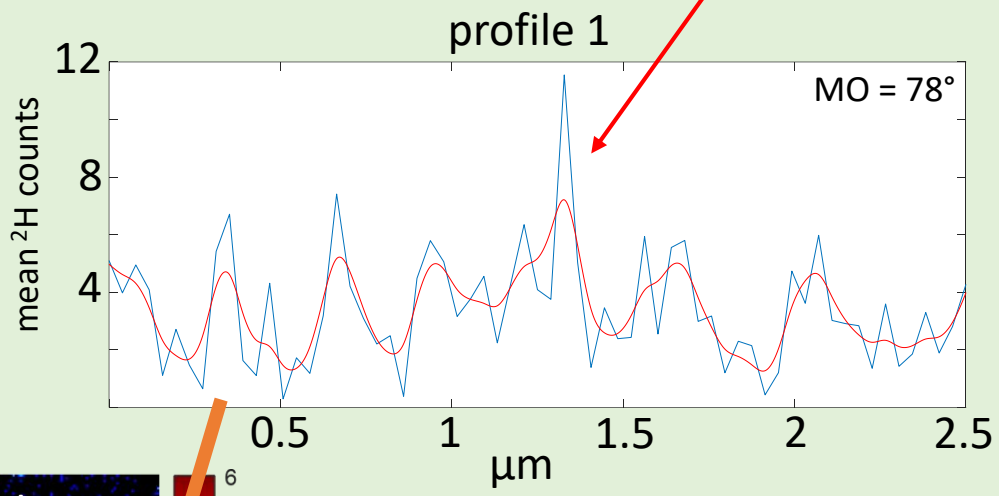
Misorientation angle across boundary

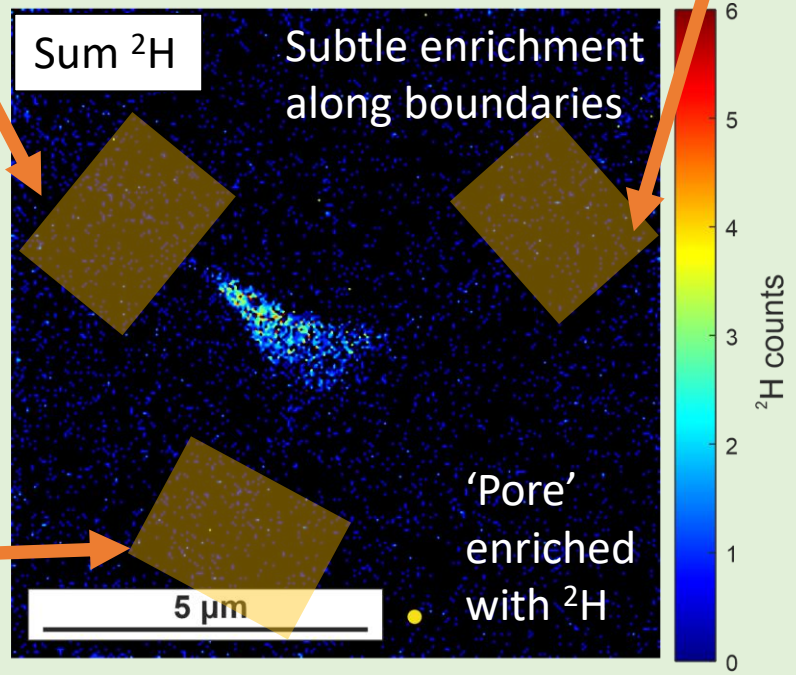


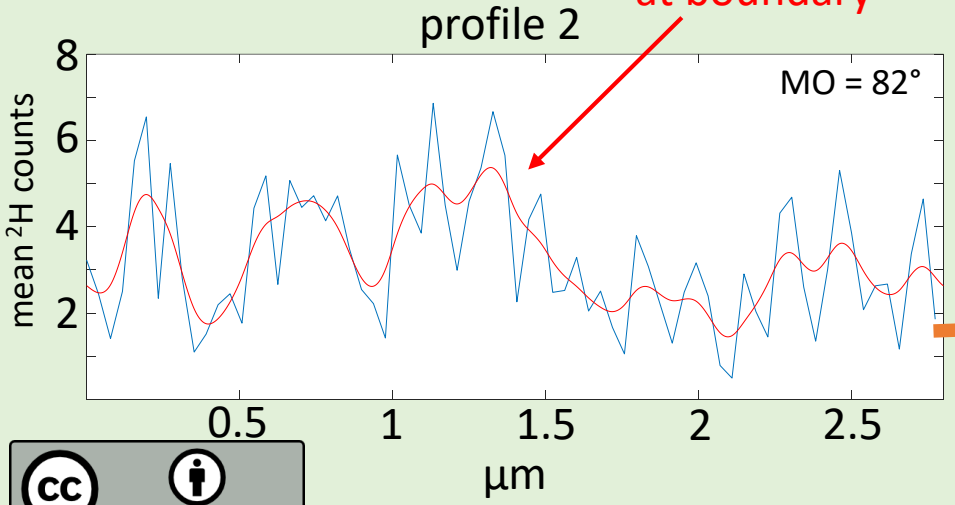
NanoSIMS results site 3









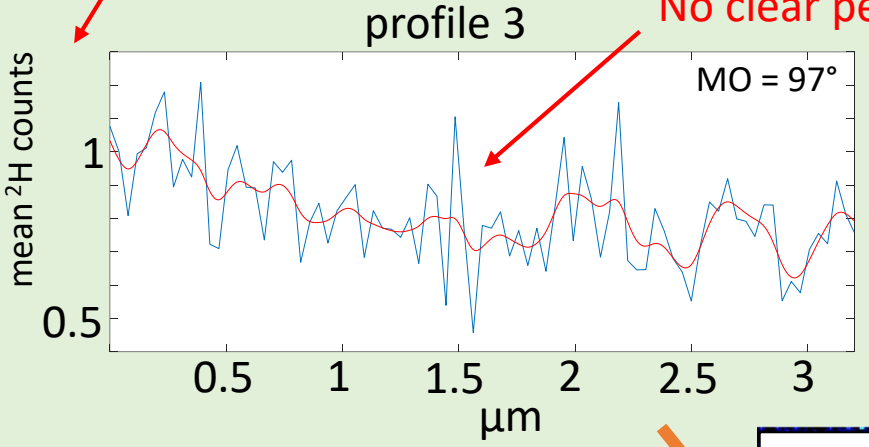


- 1000 frames
- 256 x 256 pixels
- Beam diameter: 200 nm
- Line width: 50 px
- / = spline fit

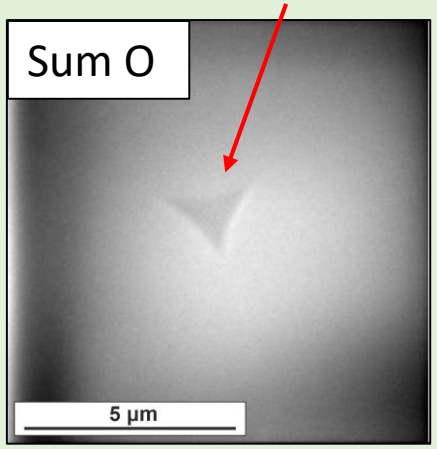
NanoSIMS results site 6

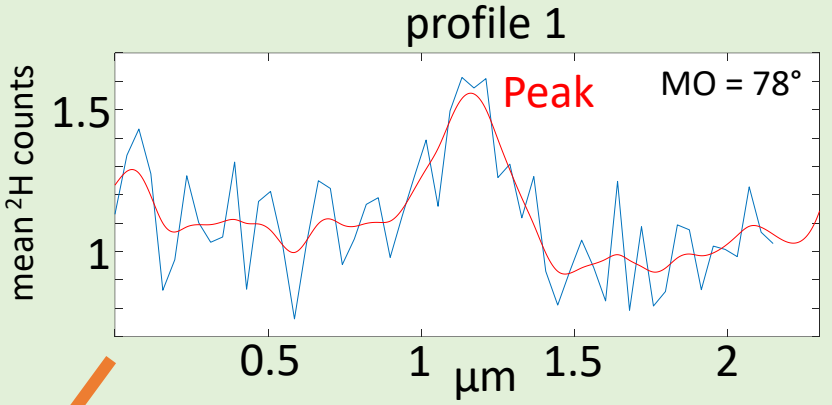
Scale shows signal much weaker than at site 3

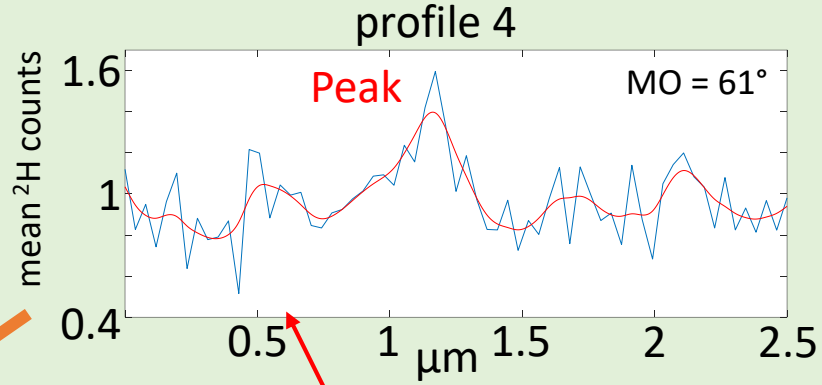
No clear peak



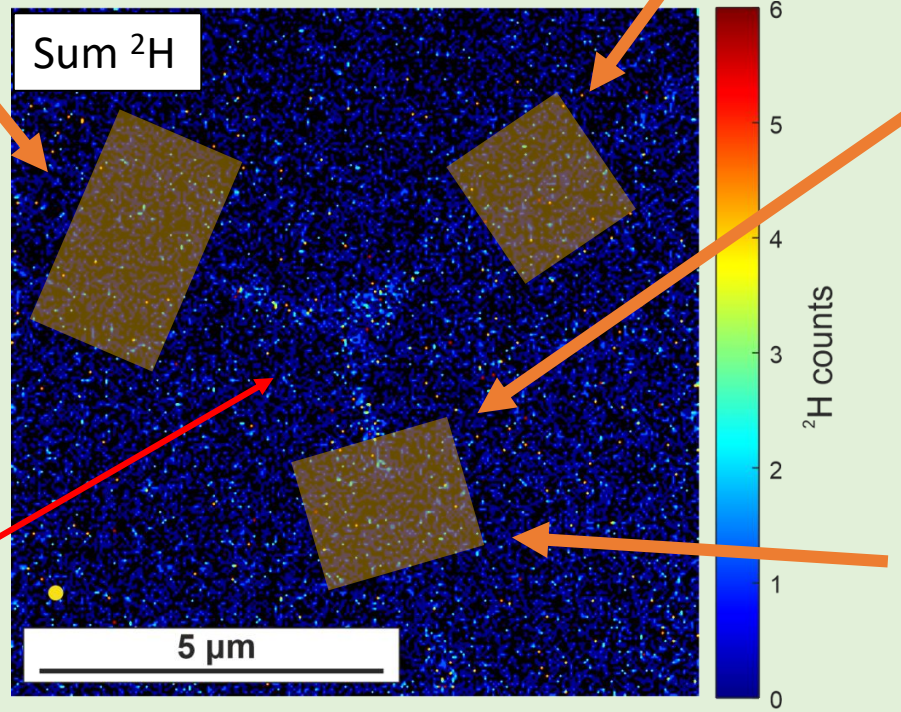
Pore? Melt pocket?





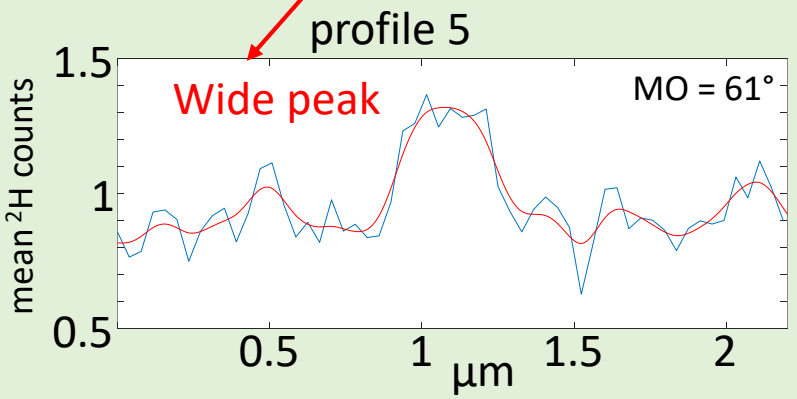


- 1000 frames
- 256 x 256 pixels
- Beam diameter = 200 nm
- Line width = 50 px, except profile 5 (100 px)
- / = spline fit



Shape of 'pore' in sum O map and sum ^{2}H map is slightly different

Same boundary, different line width: upper = 50 px, lower = 100 px



We can use boundary profile data to estimate a partition coefficient for ^2H between boundary and lattice

$$D^H_{bound/lat} = \frac{\pi\left(\frac{B_d}{2}\right)^2}{B_d\delta} \times \left(\frac{H^c_{tot}}{H^c_{lat}} - 1\right) + 1$$

beam area

max value of ^2H in boundary profile

boundary area

mean value of ^2H in lattice

B_d = beam diameter
δ = grain boundary width

Site	Boundary profile	B_d (nm)	δ (nm)	H^c_{tot} (counts)	H^c_{lat} (counts)	***D***
3	1	200	1	0.2315	0.064	**412.1**
6	1	200	1	0.8213	0.5455	**80.4**
6	4	200	1	1.0037	0.584	**113.9**
6	5	200	1	0.8889	0.5875	**81.6**

Assumption of boundary width based on TEM results in Hiraga et al (2002)

How do our values of *D* compare with previous studies?

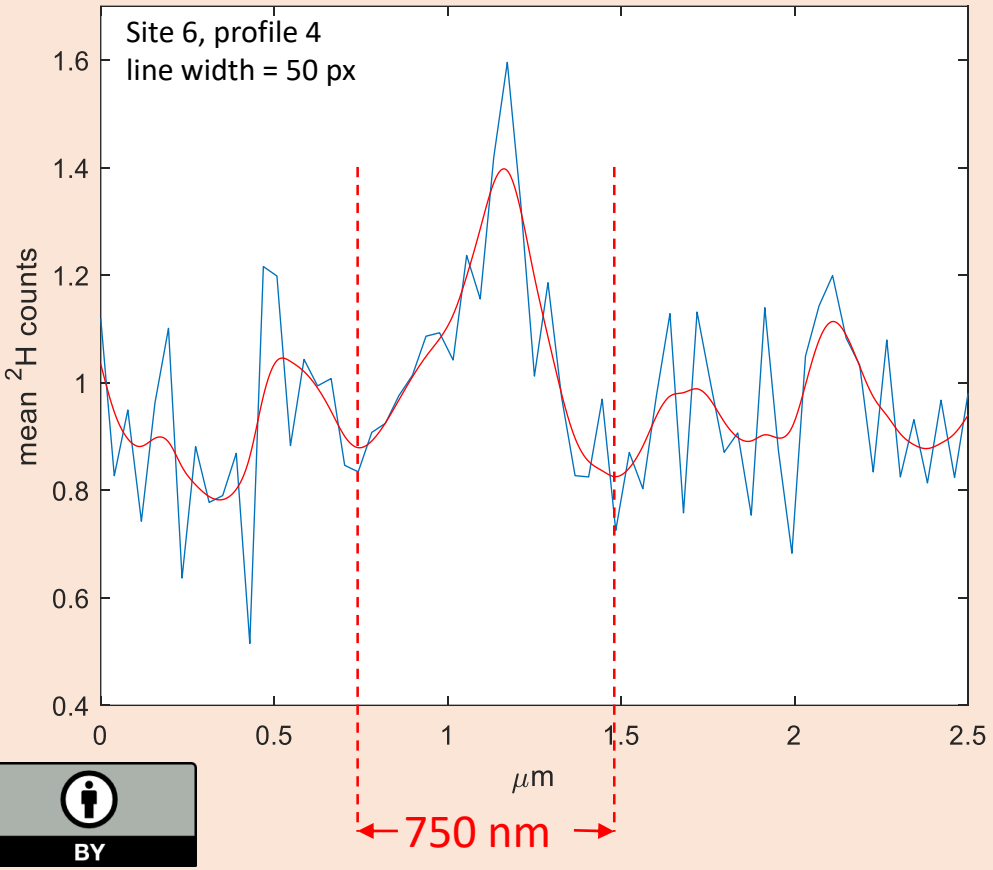
To our knowledge, there are no previous studies that report partition coefficients for ^{1}H or ^{2}H in olivine from (nano)SIMS

Study	Boundary phases	Element/compound partitioned	Method	D (boundary conc/lattice conc)
This study	olivine-olivine	^{2}H	NanoSIMS	10^{1} - 10^{2}
Hiraga et al 2004	olivine-olivine, no melt	Ca	STEM/EDX	10^{1} -10^{2}
Hiraga and Kohlstedt 2007	diopside-melt	various incompatible elements	EPMA/STEM/EDX	~10^{0} - 10^{1}
Sommer et al 2008	olivine-spinel	H_2O	Synchrotron FTIR	Actual D not reported, but ~140 ppm reported in lattice far from interface, 200-440 ppm 15 µm away from boundary, ~800 ppm closest to boundary, so 800/140 = ~5-6 (represents minimum value). Not AT the boundary, but in lattice region closest to boundary
Fei et al 2015	Olivine-olivine	H_2O	Synchrotron FTIR	~520

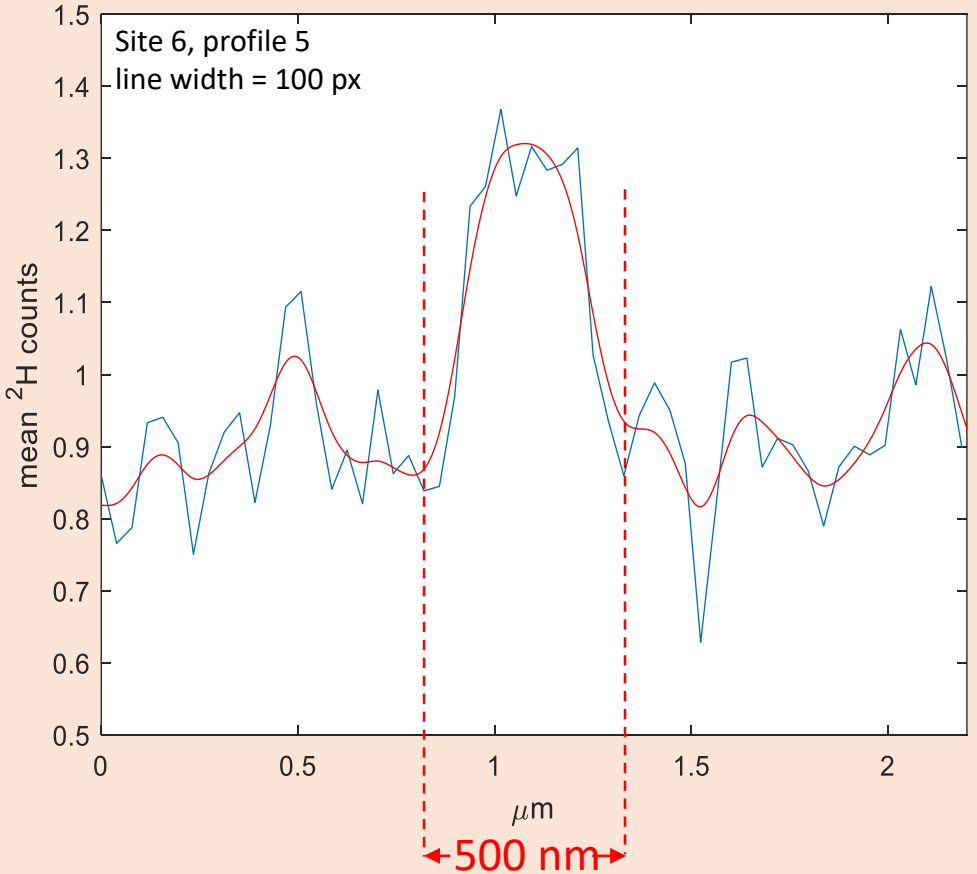
Issue with beam width vs boundary width

- Weak ^{2}H signal means we needed to use relatively wide aperture (D1-3), resulting in a beam width of 200-250 nm
- Angle of drawn boundary profile to actual boundary also important – if not perpendicular would result in wider, flatter peak

➢ Wide beam results in peak >> grain boundary width (~1 nm):



➢ Peak resolved more clearly in profiles constructed from averaging over a greater boundary length:



Conclusions and implications

- NanoSIMS was successfully used to image partitioning of D_2O between grain interiors and the grain boundary *region* at some, but not all, analysed olivine-olivine boundaries
- No clear relationship was observed between misorientation angle and recorded ^2H signal (but more boundaries need to be analysed)
- Partition coefficients calculated from the data suggest that some boundaries are enriched in ^2H by 2-3 orders of magnitude compared to grain interiors
- Boundaries at which partitioning was observed yield partition coefficients of the same order of magnitude as previous studies on other elements, suggesting that boundary environments can be enriched in ^2H relative to grain interiors at equilibrium
- These observations concur with the conclusions of previous studies, adding to the weight of evidence that suggests grain boundaries can act as a substantial water reservoir in Earth's mantle

Future work (samples)

- Could enriched region in ^{2}H maps be a melt pocket (i.e. glass)?
  - ➢Secondary electron imaging to analyse topography – pore or filled?
  - ➢EDX to analyse composition – if Ca-rich, suggestive of melt
- Could observed peaks on boundaries also be melt/glass lining?
  - ➢TEM foils cut across the grain boundary to analyse material at atomic scale – are boundaries tight or porous; are they lined with non-crystalline material?
- To date, only fully analysed one experimental condition. Need to perform same analysis on two other samples synthesised at
  - ➢T = 1000 °C, P = 2GPa, t = 0.1 h
  - ➢T = 1200 °C, P = 2 GPa, t = 24 h

Short experimental timescale so equilibrium partitioning between boundary and lattice may not have been reached; important for comparison

At these conditions, production of melt in experiments is extremely unlikely

Future work (technique)

- For greater spatial resolution across grain boundaries, use of a smaller aperture would be required, for which the ^{2}H signal in such synthetic samples would need to be amplified
- Was lack of observed partitioning at some boundaries due to genuine lack of partitioning, or because degree of partitioning was beyond the resolution limits of the technique, or masked by matrix effects? Higher resolution analyses and characterisation of grain/boundary (mis)orientations may help answer such questions