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Growth, replacement and element diffusion in garnet

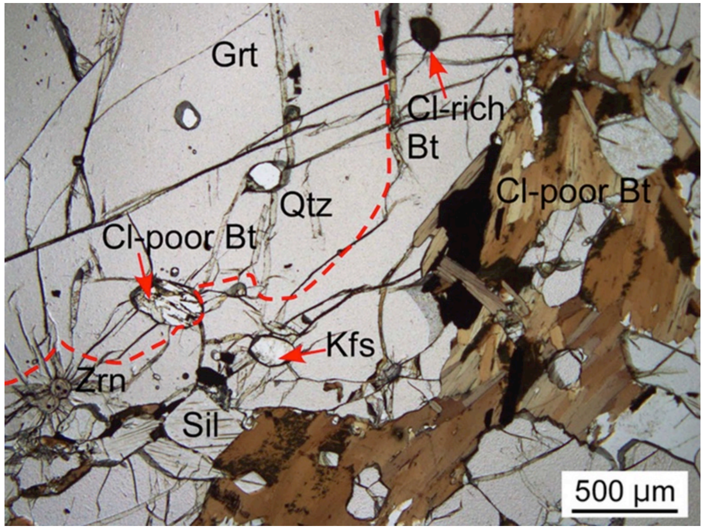
Part II: OXYGEN DIFFUSION

Daniela Rubatto[1] and collaborators at ETH-Zurich, Uni Bern, Uni Lausanne, ANU, Columbia University

1. *University of Bern, Institute of Geological Sciences, Switzerland*
2. *Institut de Sciences de la Terre, University of Lausanne, Switzerland*

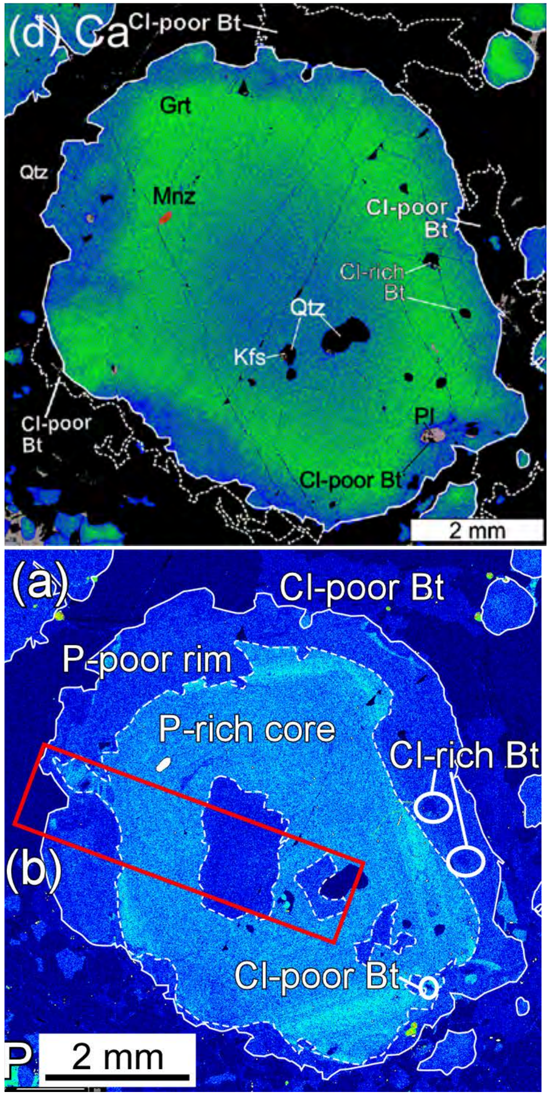
Element diffusion in garnet

Granulites, Sør Rondane, East Antarctica
Pelitic gneiss: Grt-Sill-Bt



✓ Relaxed major element zoning

✓ Step-wise P zoning

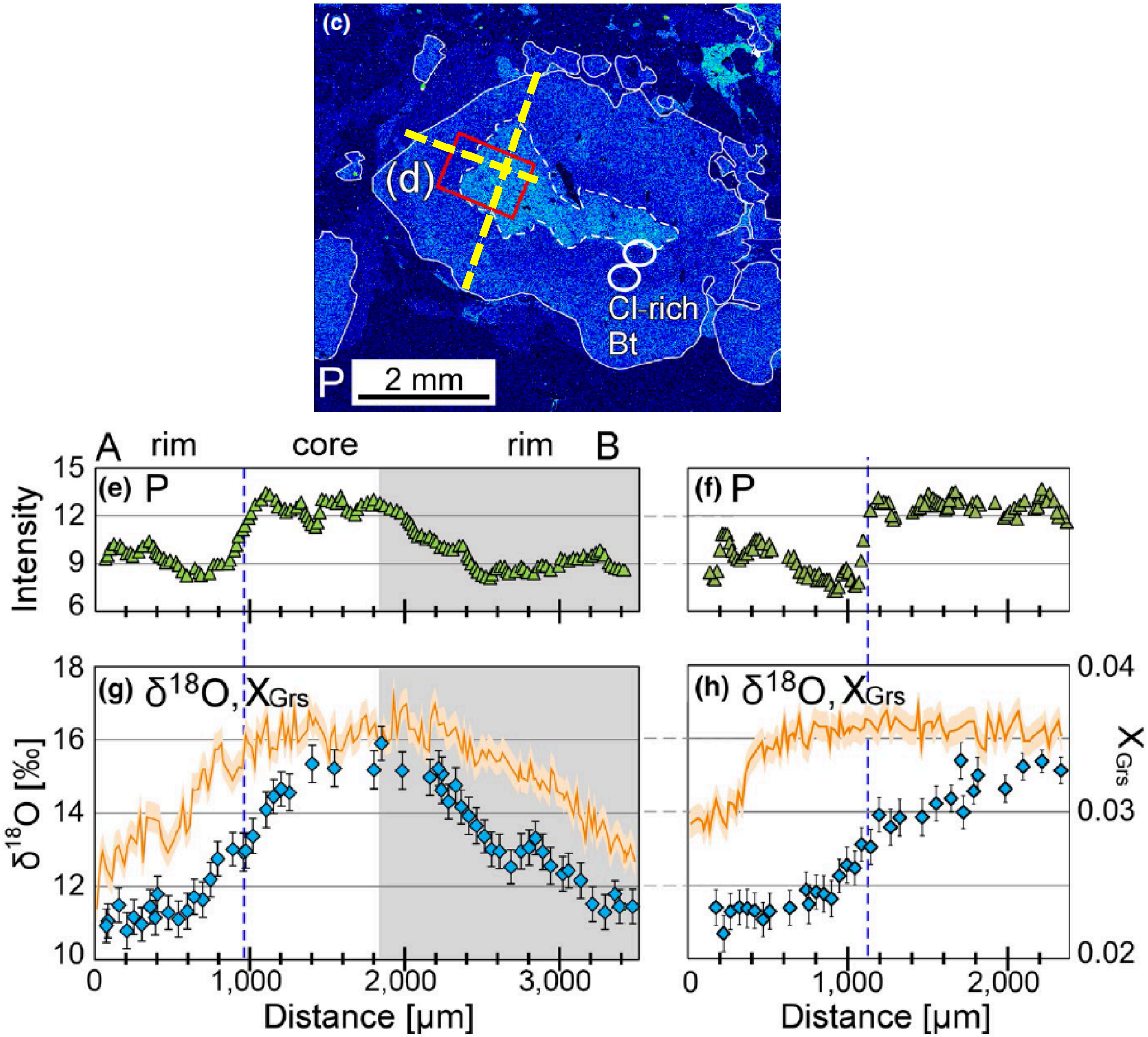


Peak conditions 850°C, 1.1 GPa
Garnet rim growth 800°C, 0.8 GPa

Higashino et al. 2013

- ✓ Veins indicating penetration of Cl-rich brines
- ✓ Fluid infiltration at 800°C

Oxygen diffusion in garnet



- ✓ Relaxed major element zoning
- ✓ Step-wise P zoning
- ✓ Symmetric $^{18}O/^{16}O$ zoning

Oxygen isotopes

- Preserved $\delta^{18}O$ zoning at 800°C!
- Core - rim zoning $\delta^{18}O$ = 15.5 to 11.0 ‰
- Input of external fluids

Higashino, Rubatto, Kawakami, Bouvier, Baumgartner 2019

Oxygen speedometry

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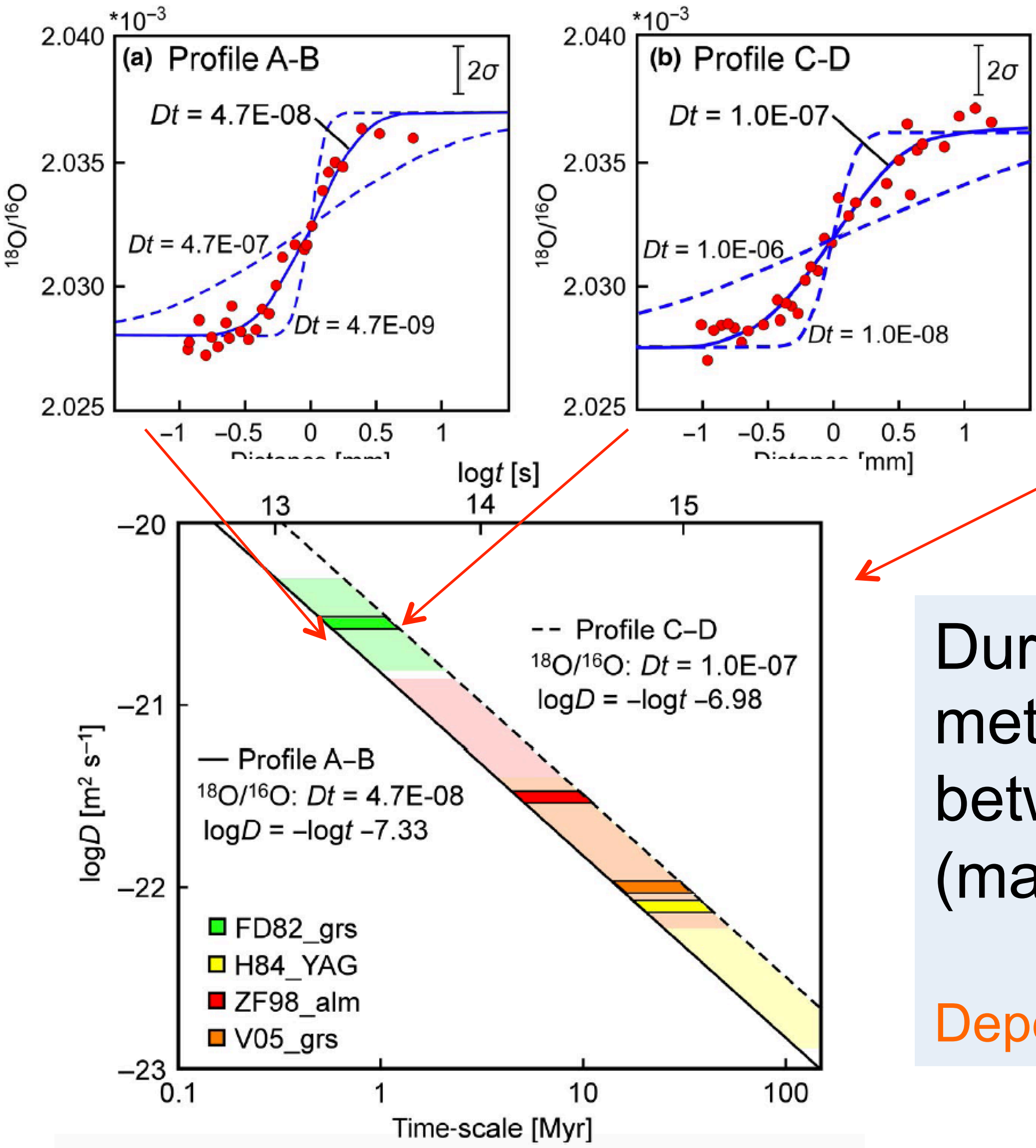

Data fitted to Fick´s second law (Crank, 1975)

$C = C_{min} + 0.5\,(C_{max} - C_{min})\ erfc\,[x / (4Dt)^{0.5}]$

Duration of high T metamorphism (800°C) between 0.5-40 Ma (maximum)

Depends on diffusion coefficient D

Higashino, Rubatto, Kawakami, Bouvier, Baumgartner 2019

Oxygen diffusion experiments

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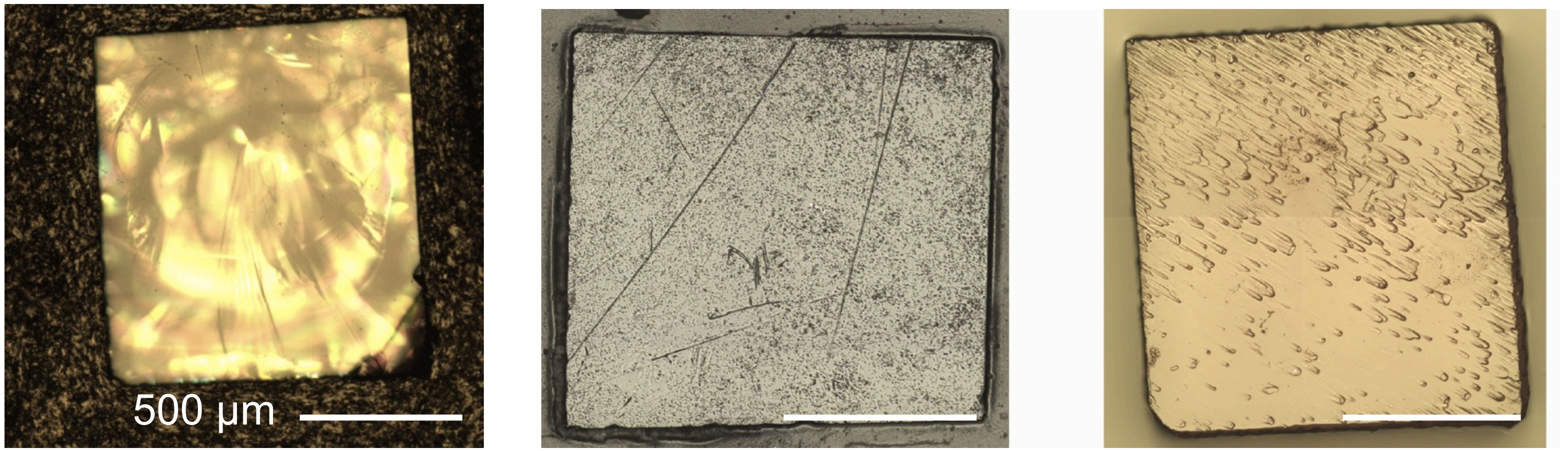
Oxygen diffusion in garnet

Experimental study using YAG ($Y_3Al_5O_{12}$) and pyrope ($Mg_3Al_2Si_3O_{12}$) garnet in a ^{18}O enriched matrix

1. Gas furnace with Ar flux 1500–1600°C
2. Piston cylinder 900–1600°C, 1.0–2.5 GPa, dry and wet

Recovered garnet cubes after experiment

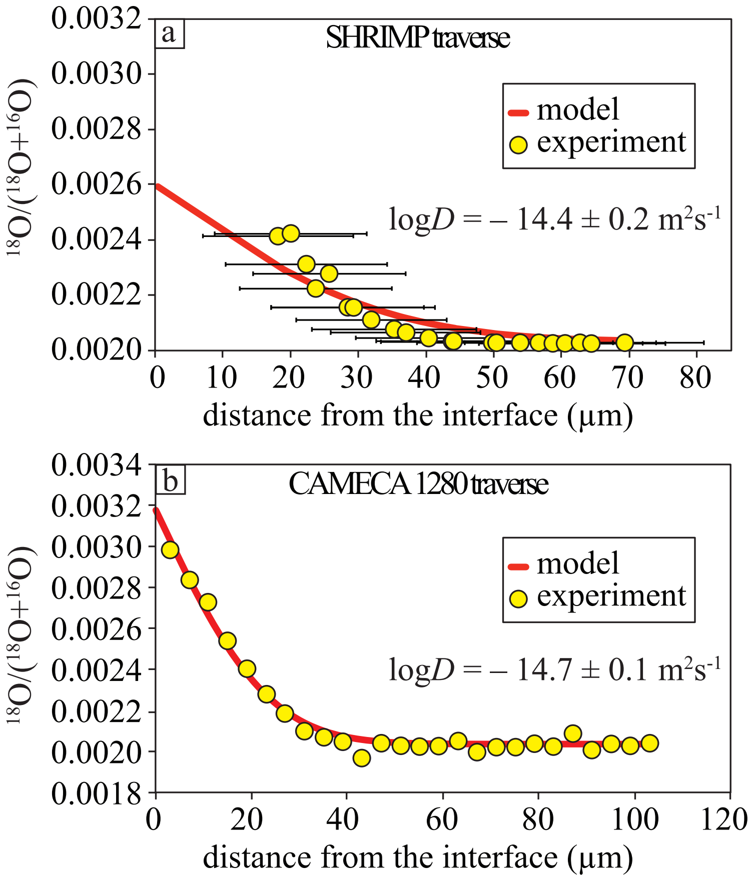


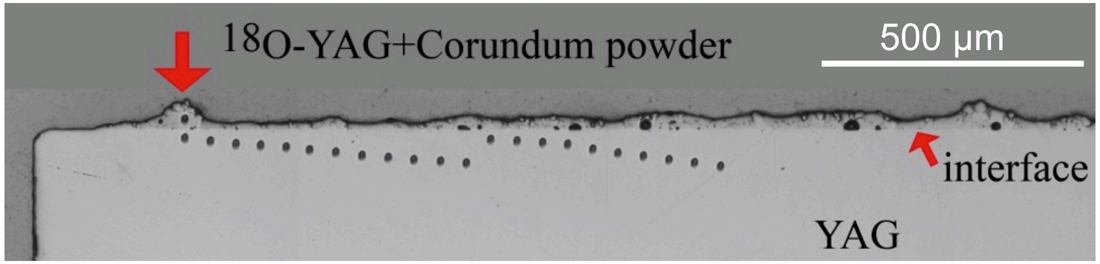
Scicchitano, Jollands et al. 2021

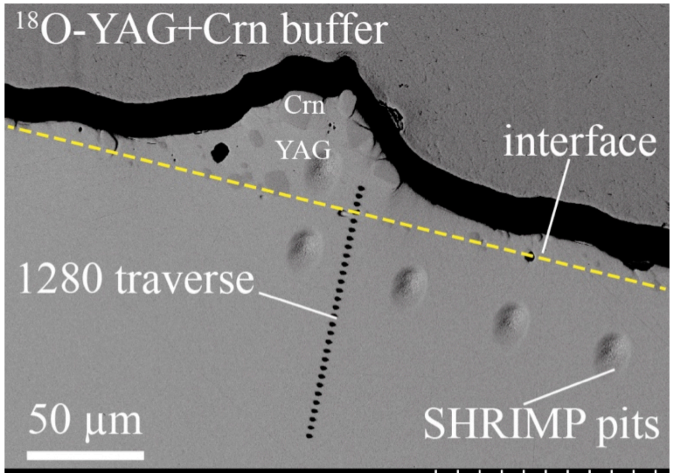
Oxygen diffusion in garnet

Measurement of $^{18}O/^{16}O$ with three methods

1. SIMS (SHRIMP and Cameca 1280) traverse – resolution 15–3 microns





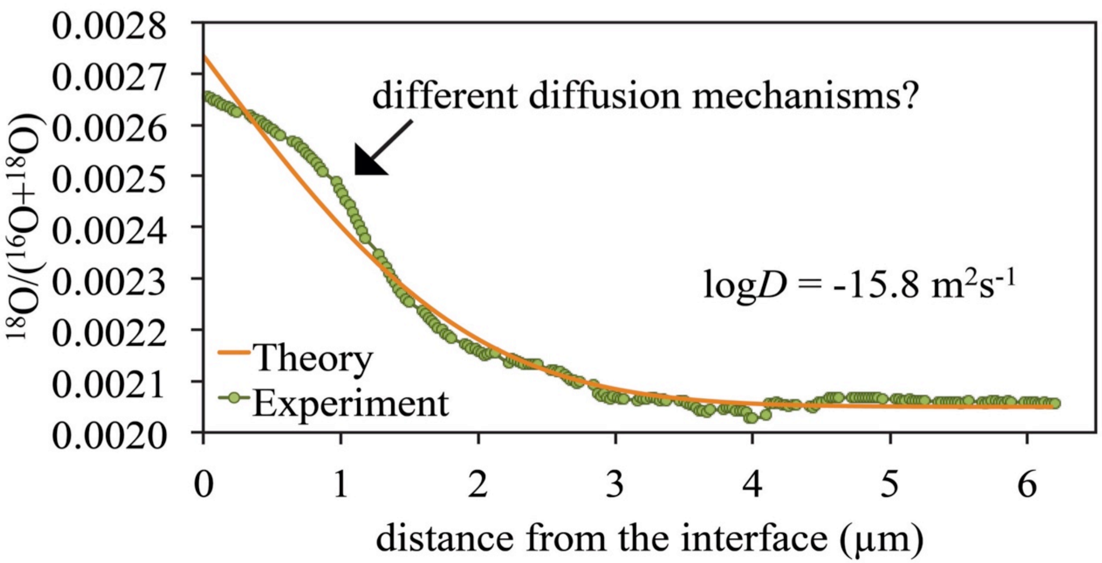


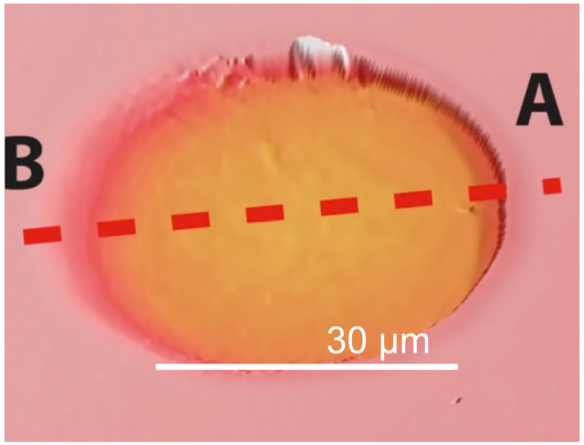
Scicchitano, Jollands et al. 2021

Oxygen diffusion in garnet

Measurement of $^{18}O/^{16}O$ with three methods

2. SIMS (SHRIMP and Cameca 1280) depth profiling – resolution ~ 20 nm



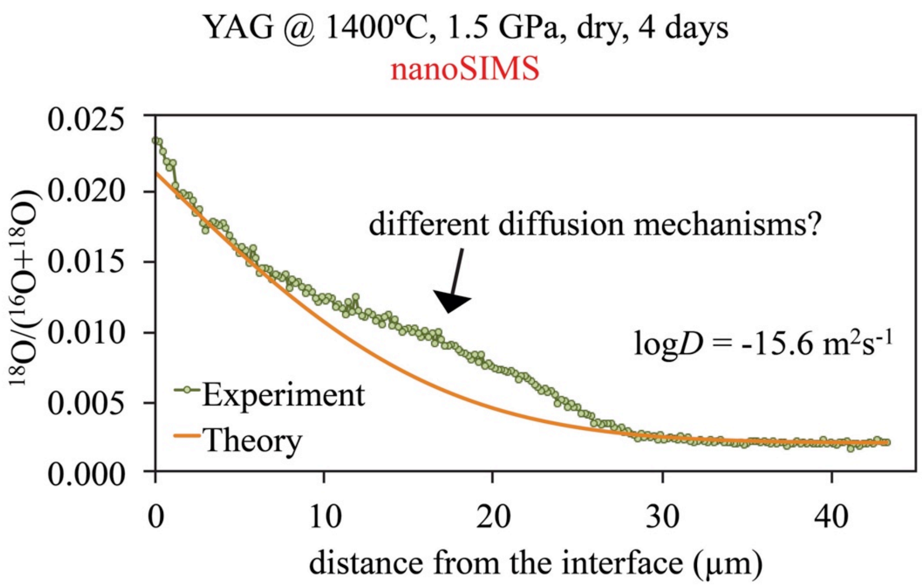


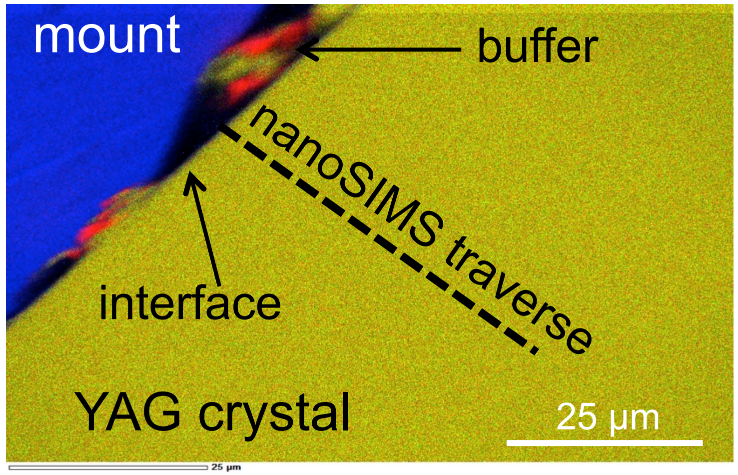
Scicchitano, Jollands et al. 2021

Oxygen diffusion in garnet

Measurement of $^{18}O/^{16}O$ with three methods

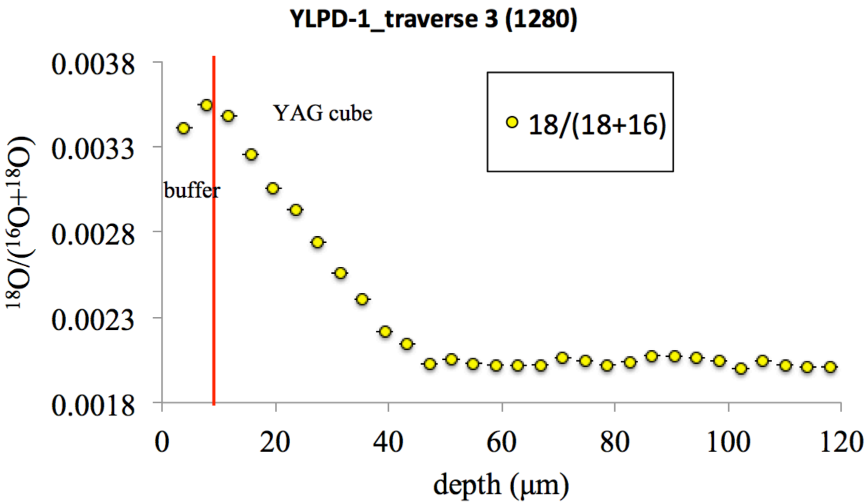
3. nanoSIMS traverses – spot resolution 200 nm





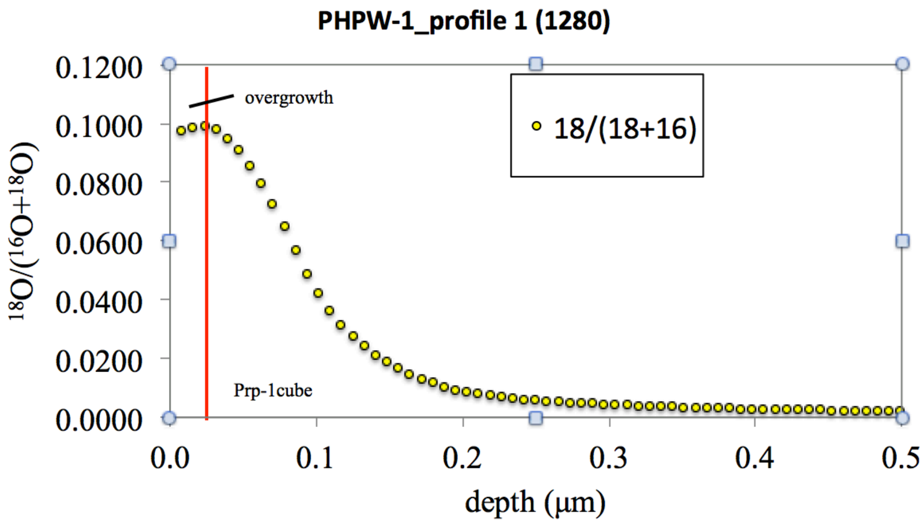
Scicchitano, Jollands et al. 2021

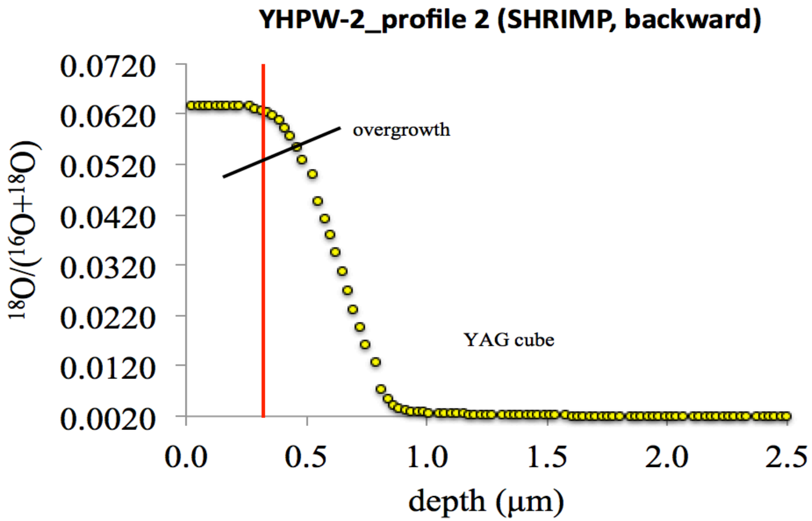
Different types of profile



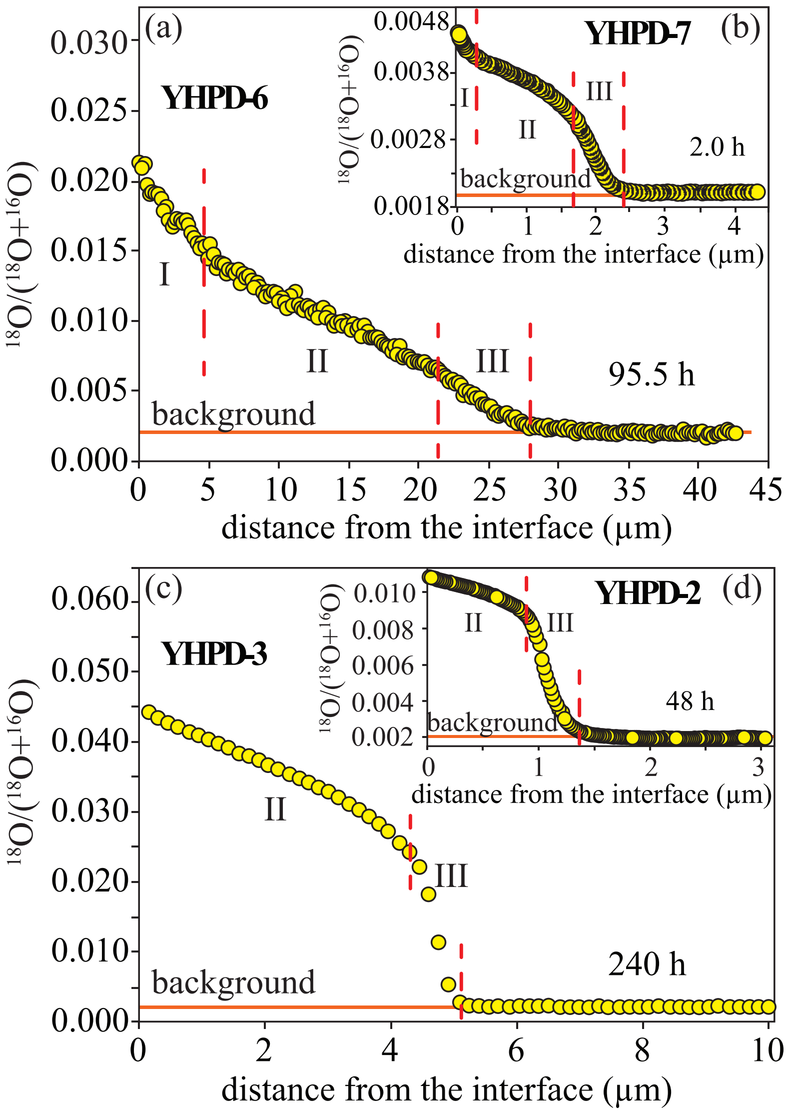
1. Error function profiles

In LP–HT runs, in HP–LT "wet" runs



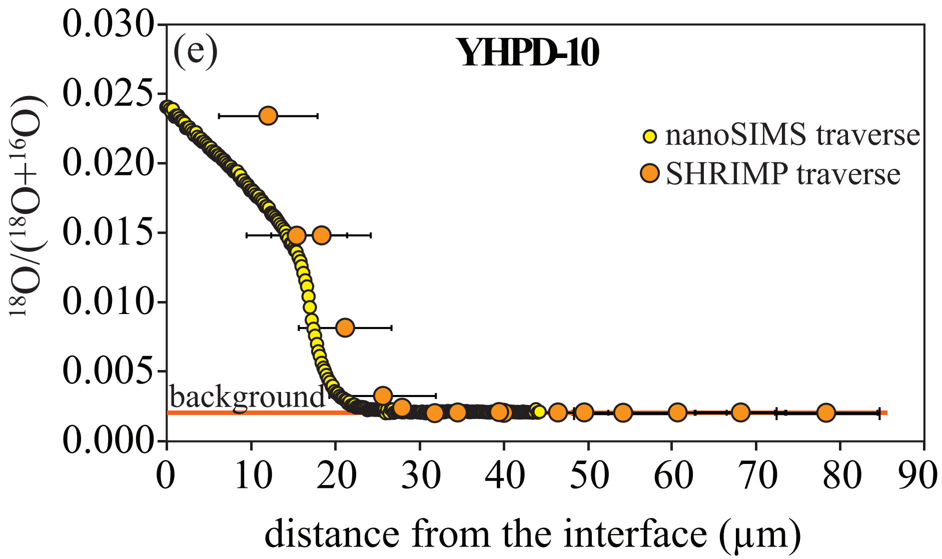


Different types of profile

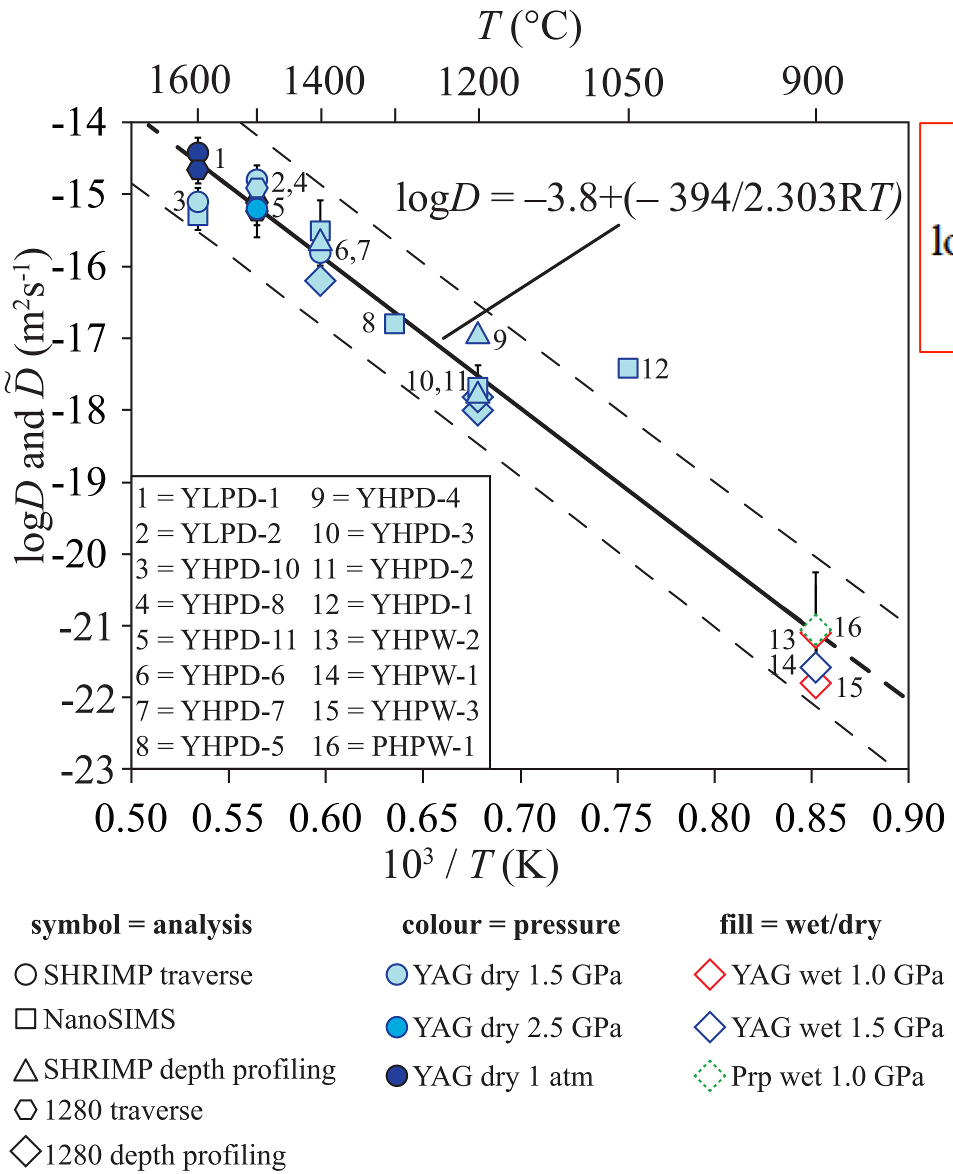


2. Stepped profiles

In all HP “dry” experiments, 1 excl.



Results, first approximation

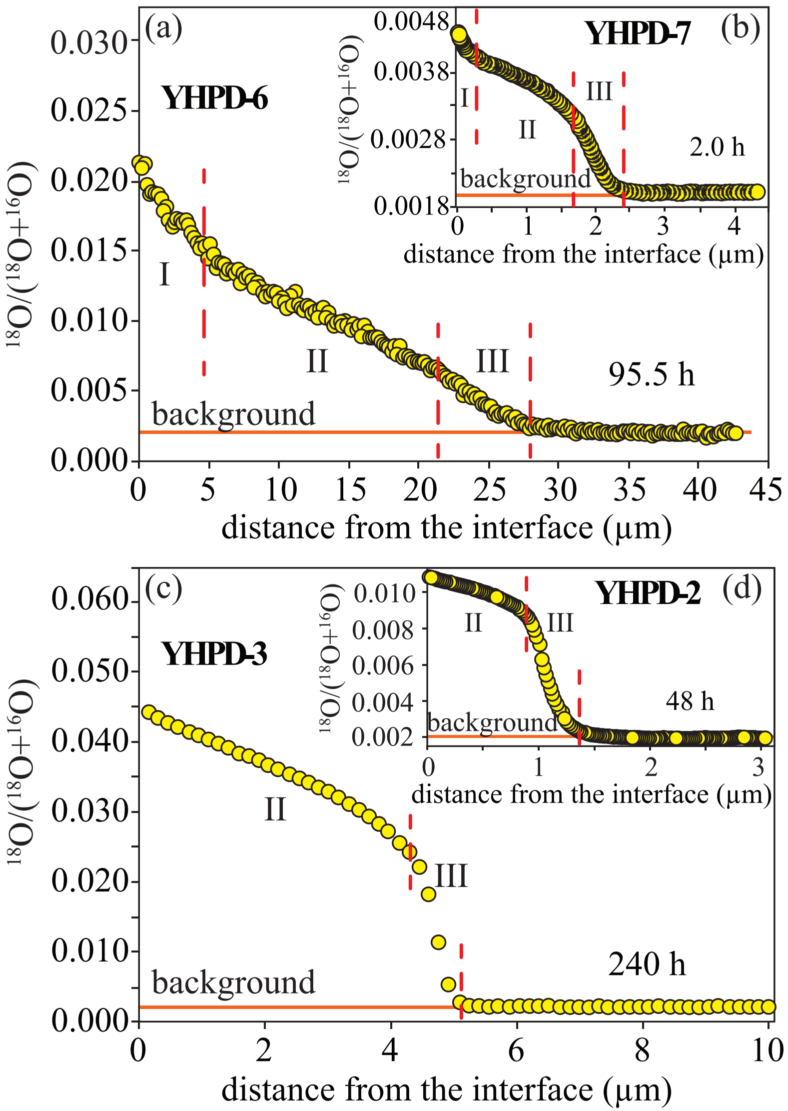


$$\log\tilde{D}\ \mathrm{m^2 s^{-1}} = -3.8\ (\pm 0.7) + \left(\frac{-394\ (\pm 19)\ \mathrm{kJmol^{-1}}}{2.303RT}\right)$$

Full dataset (partial fitting)

No composition effect
See no H_2O effect
Cannot estimate P effect

Results: stepped profiles



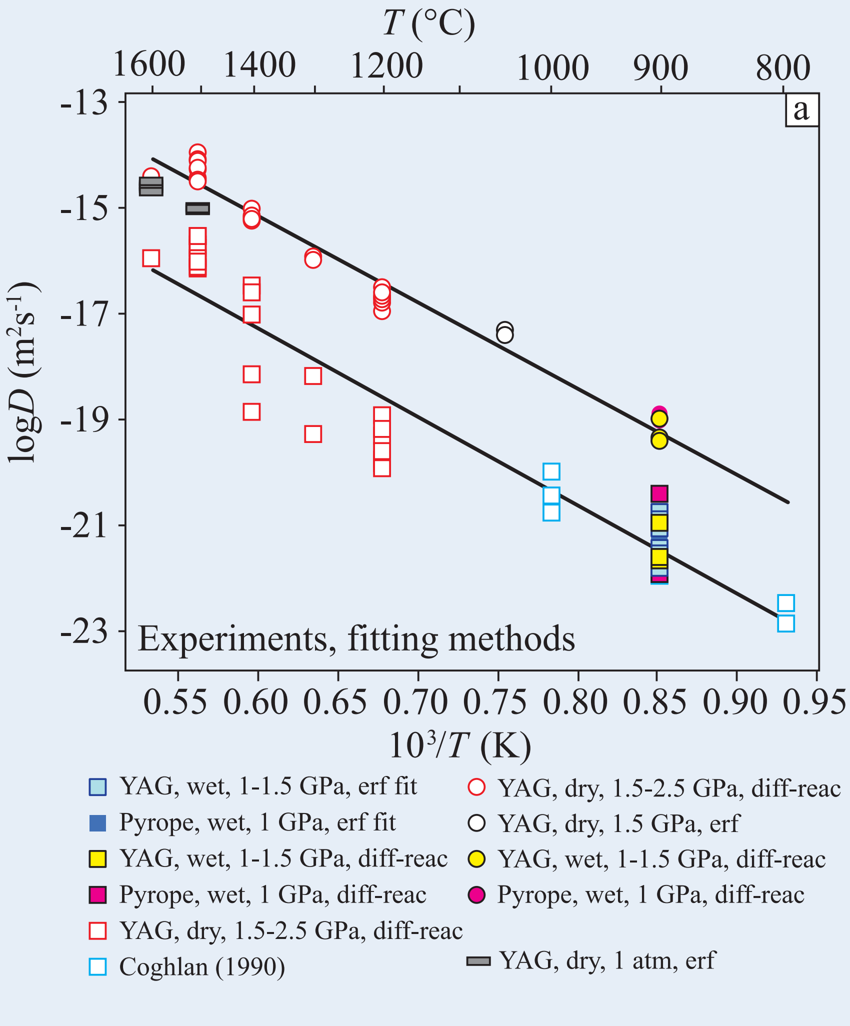
Overgrowth + diffusion is unlikely

Not concentration-independent diffusion on a single site

Two diffusion mechanisms likely fast pathway + slow pathway

Diffusion on vacancy + interstitial

Results: two mechanisms



Two diffusion mechanisms likely
fast pathway + slow pathway

Diffusion on vacancy + interstitial

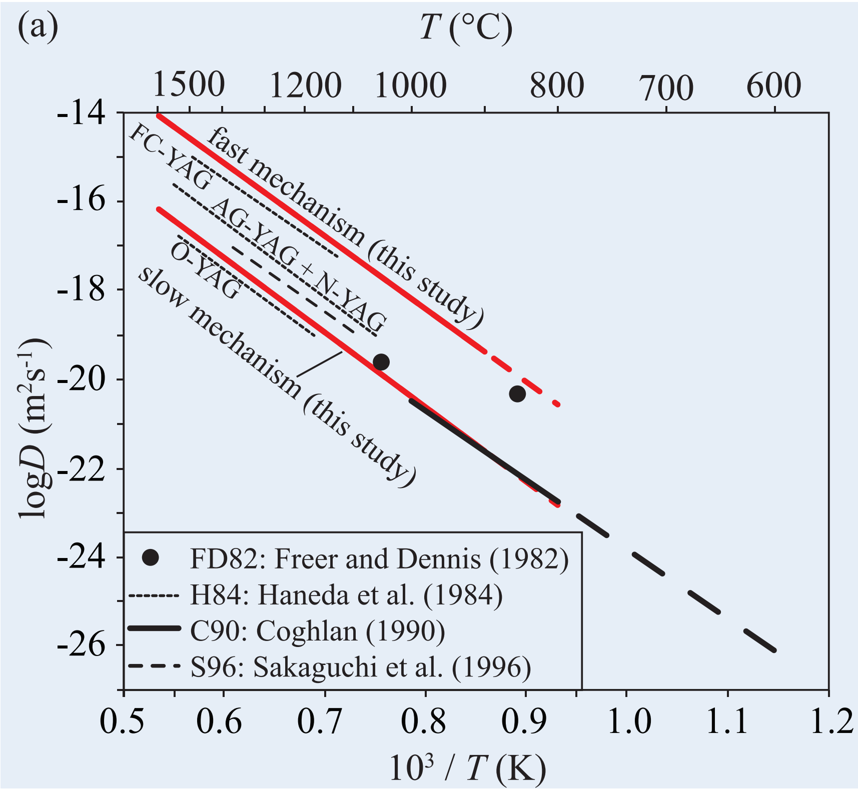
slow (most profiles)

$$\log D \ \mathrm{m^2 s^{-1}} = -7.2\ (\pm 1.3) + \left(\frac{-321\ (\pm 32)\ \mathrm{kJmol^{-1}}}{2.303RT} \right)$$

fast

$$\log D \ \mathrm{m^2 s^{-1}} = -5.4\ (\pm 0.7) + \left(\frac{-312\ (\pm 20)\ \mathrm{kJmol^{-1}}}{2.303RT} \right)$$

Comparison to previous studies



All previous experimental/ natural/computational results fall within the range

slow (most profiles)

$$\log D \; m^2s^{-1} = -7.2\ (\pm 1.3) + \left(\frac{-321\ (\pm 32)\ kJmol^{-1}}{2.303RT} \right)$$

fast

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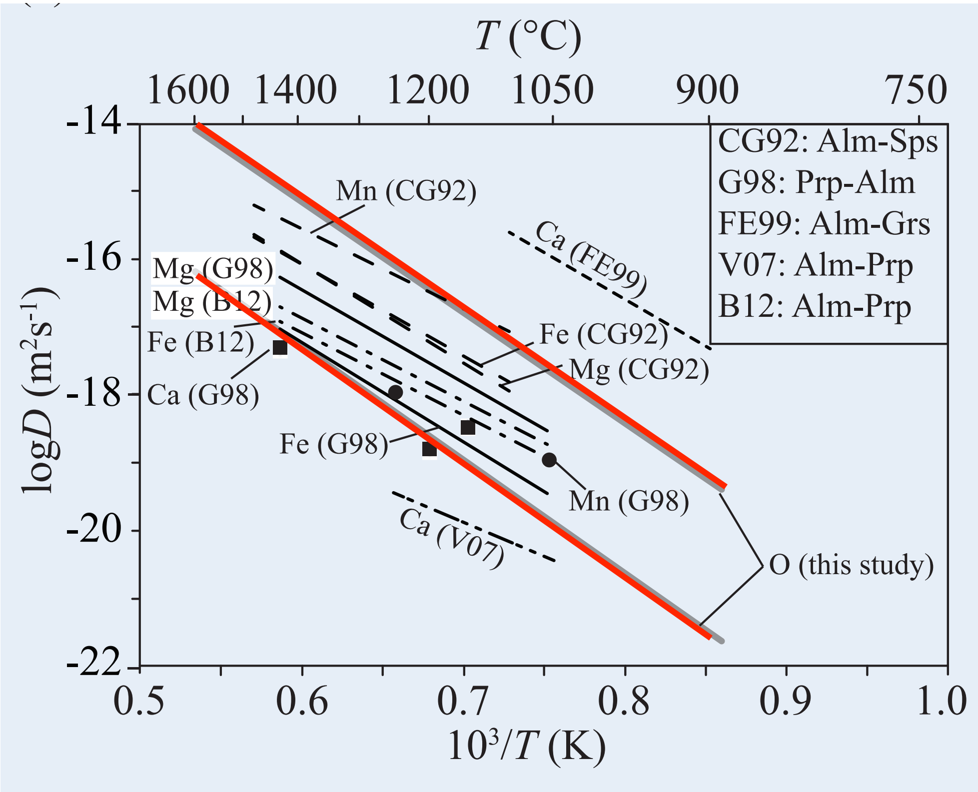
Comparison to cations



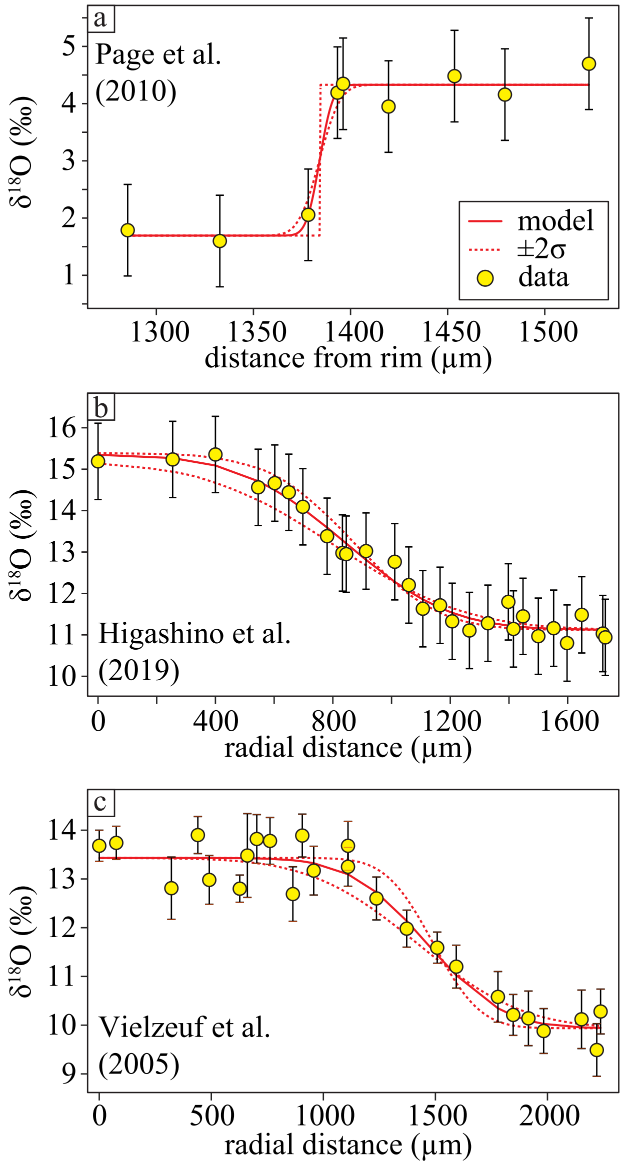
Data are not normalized to a fixed oxygen fugacity.
CG92: Chakraborty and Ganguly (1992); G98: Ganguly et al. (1998); FE99: Freer and Edwards (1999); V07: Vielzeuf et al. (2007); B12: Borinski et al. (2012).

Activation energy O > major divalent cations

⇒ Extrapolation to *T*<850 °C would result in slower O diffusivity relative to major cations

ADVANTAGE for O
- is not a multicomponent system
- is not dependent on composition

Natural data



Regional metamorphism:
Best fit = log*Dt* (m^2) of –10.8
750 °C, log*D* (m^2s^{-1}) of –24.2±0.5 = max 1.6 M.y.

Regional metamorphism:
Fit to spherical geometry = log*Dt* (m^2) = –7.4±0.2
800°C regression for the slow diffusivity gives
log*D* (m^2s^{-1}) of –22.9±0.5 (2σ) = times of 30-320 M.y.

Crustal melting:
Fit to spherical geometry = log*Dt* (m^2) of –7.5±0.3
At 800°C regression for the slow diffusivity gives
log*D* (m^2s^{-1}) of –22.2±0.4, = 4 to 50 M.y.

Conclusions

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- Garnet O zoning can be retained at high T metamorphic conditions
- Diffusion of O in garnet is regulated by two mechanisms with the slow one being the most relevant to natural settings
- Diffusion of O is likely to be slower than that of major cations
- The diffusivity of O may be a “goldilocks” case in between major and trace elements

How robust if oxygen in garnet?

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Oxygen diffusion in garnet

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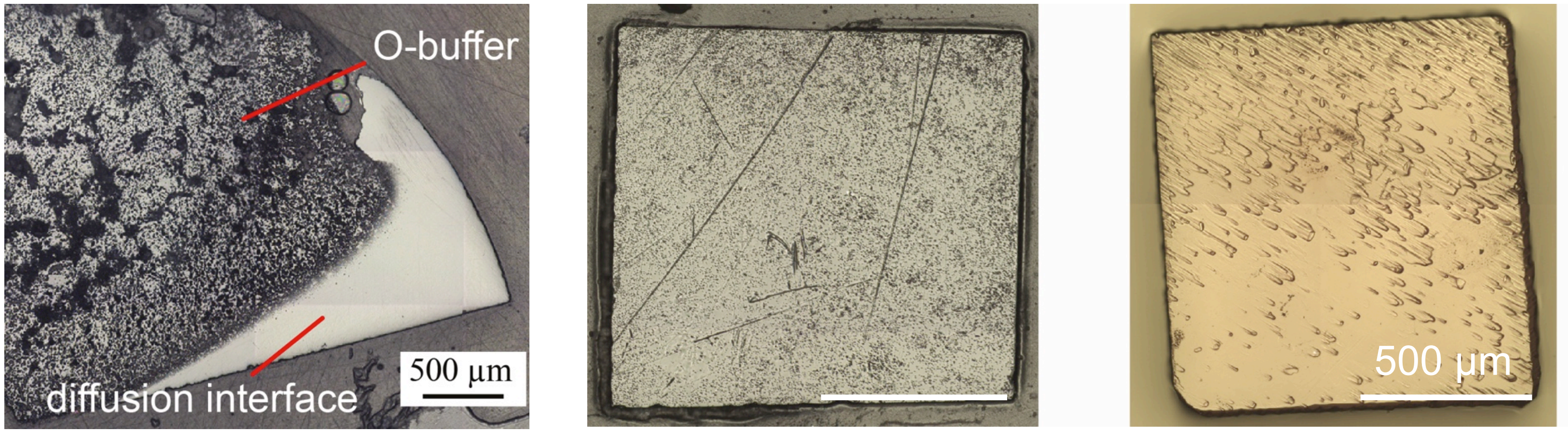
Recovered garnet cubes after experiment



M R Scicchitano, PhD thesis 2017

Pervasive fluid flow in subducted crust

Daniela RUBATTO, Thomas BOVAY, Pierre LANARI
University of Bern, Institute of Geological Sciences, Switzerland

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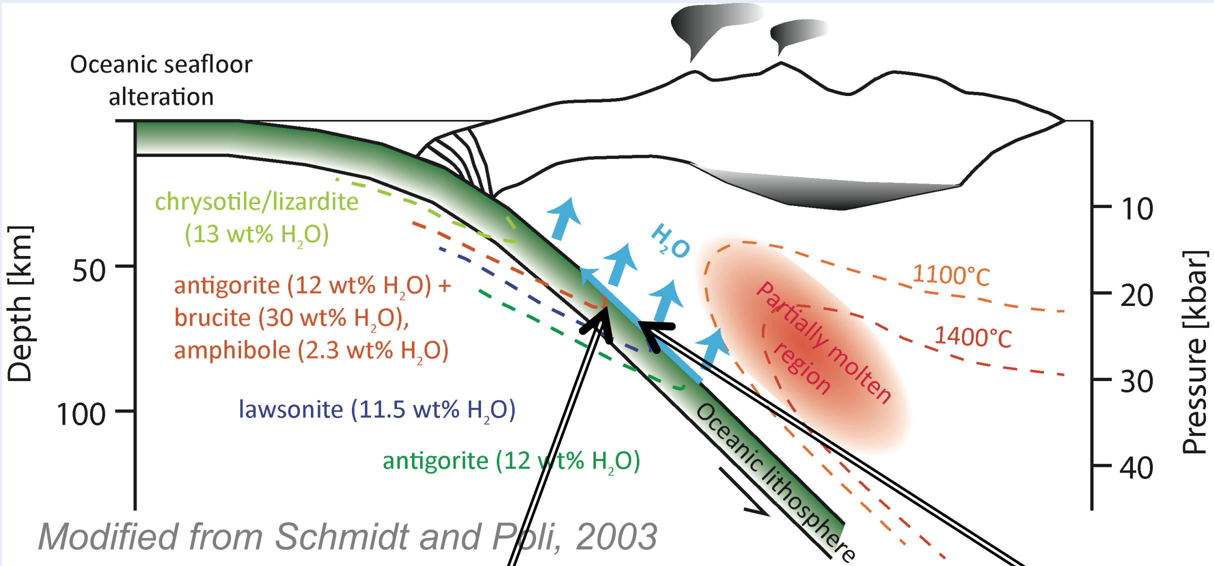
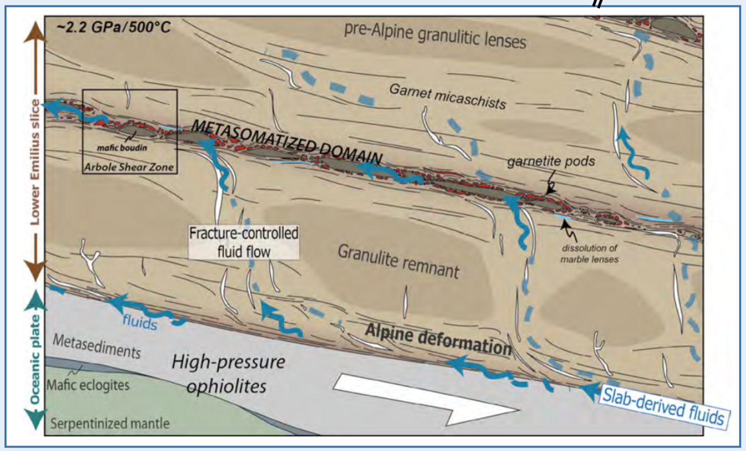
SWISS NATIONAL SCIENCE FOUNDATION

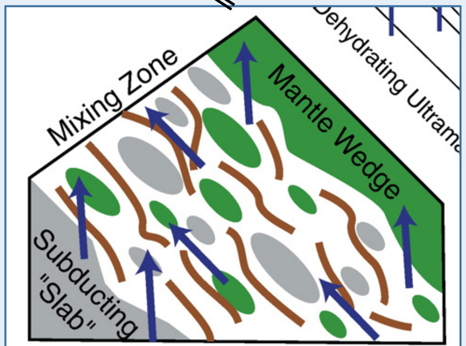


Modified from Schmidt and Poli, 2003

Fluid production is known



Angiboust et al., 2016



Zones of mechanical and metasomatic mixing, with hybridized compositions influencing "fluid" compositions

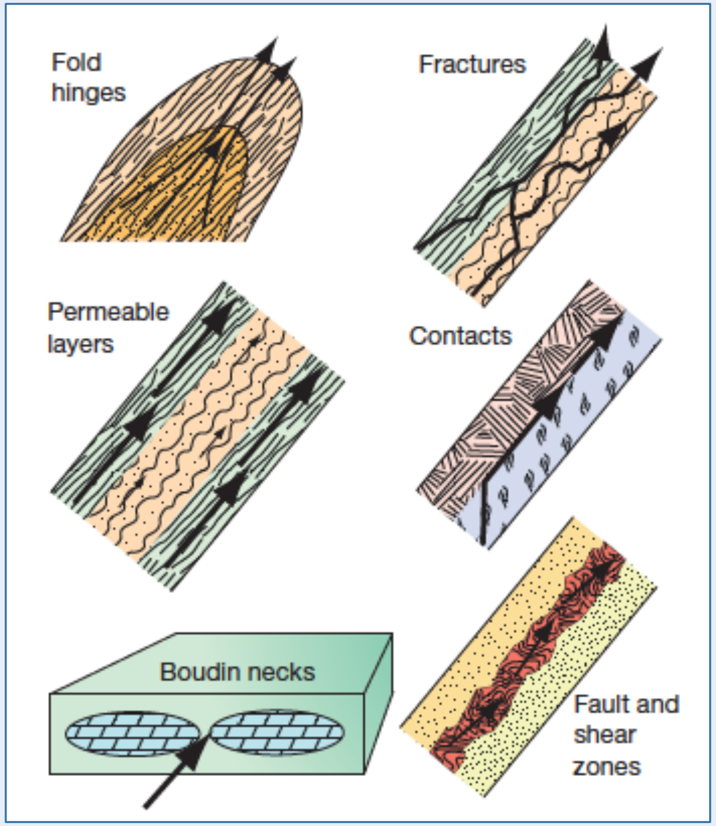
Bebout, 2007

Fluid flow dynamics??

Pervasive fluid flow in subducted crust

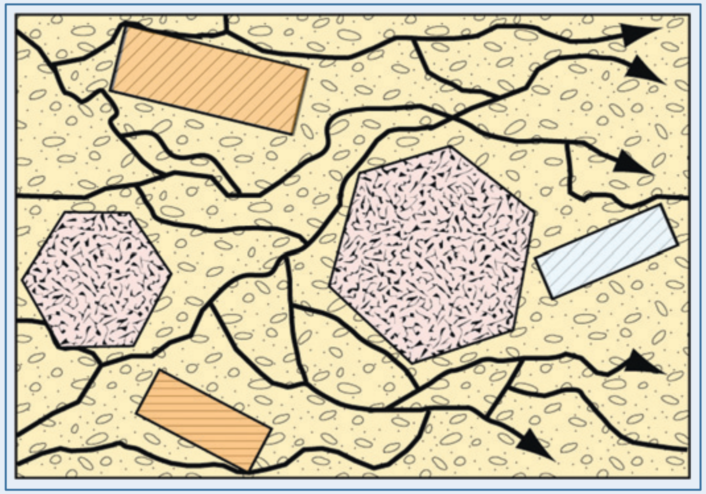
Daniela RUBATTO, Thomas BOVAY, Pierre LANARI
University of Bern, Institute of Geological Sciences, Switzerland

- **channelized**
(veins, shear zones, contacts)



Ague, 2014

- **pervasive**
(intergranular porosity)



Ague, 2014

Theodul Glacier Unit (TGU)

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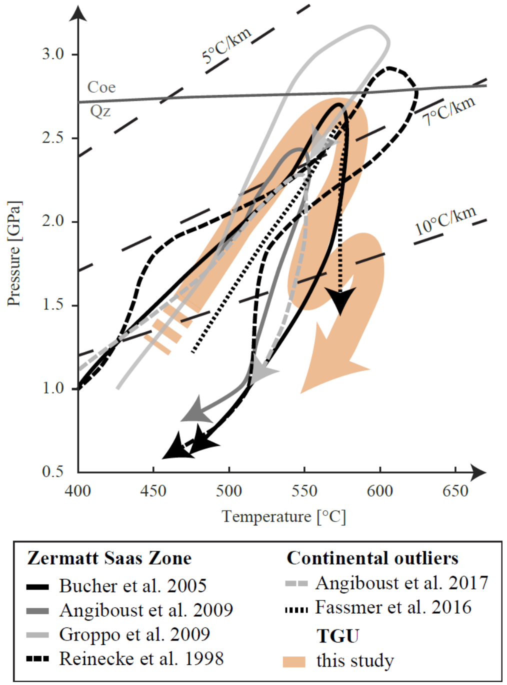
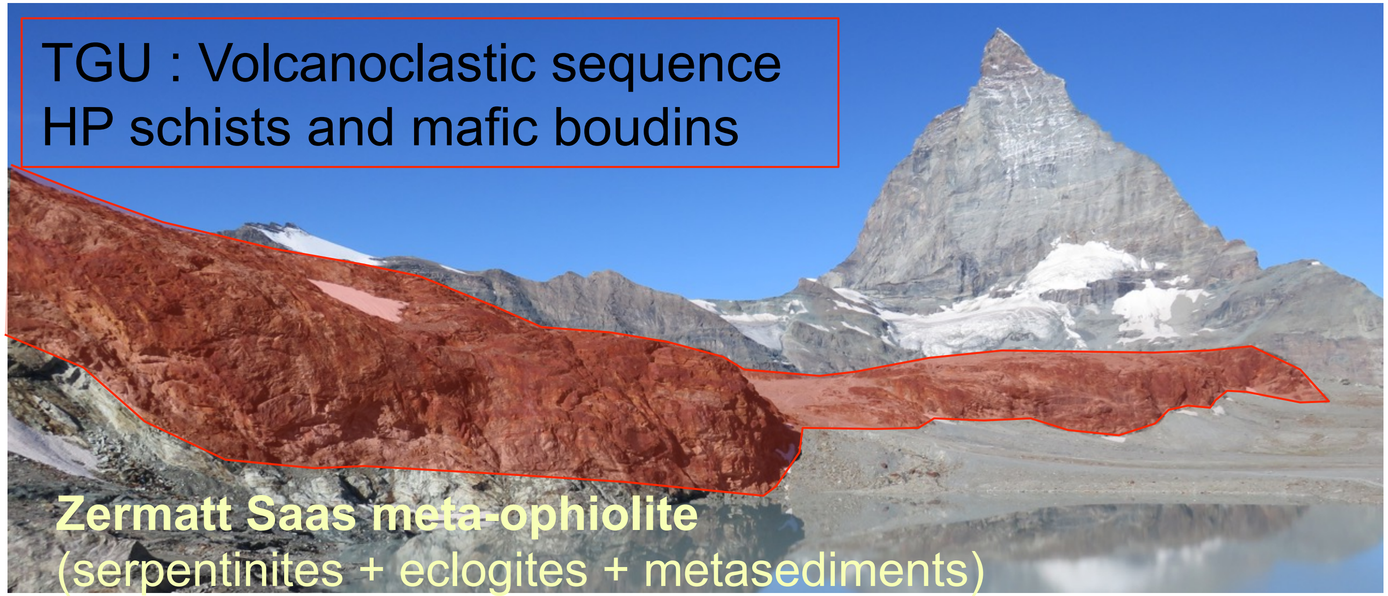
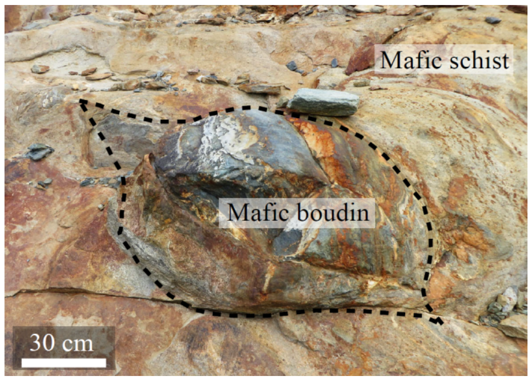
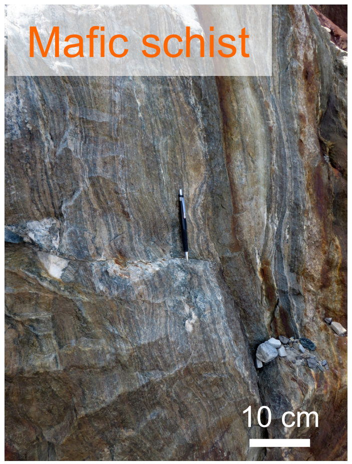
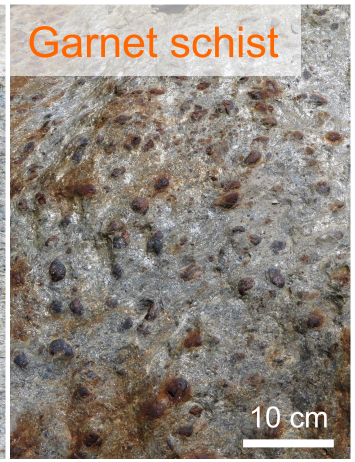
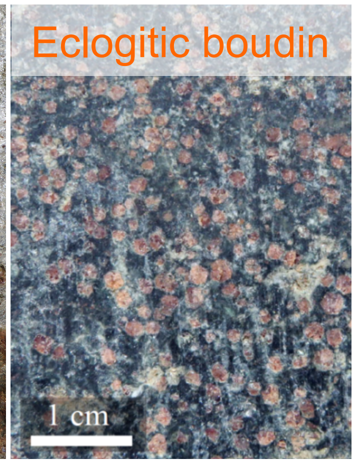










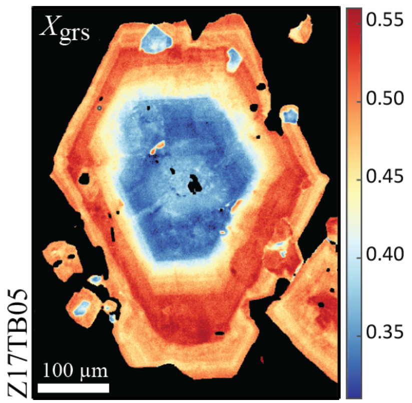


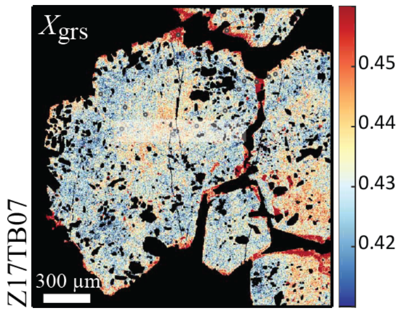
Garnet textures

Continuous zoning = continuous growth in a fractionating reactive bulk

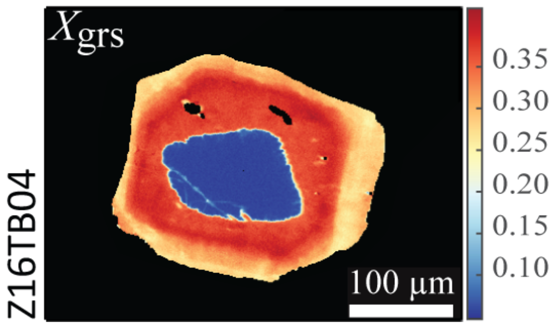
Discontinuous zoning = resorption and regrowth induced by fluids

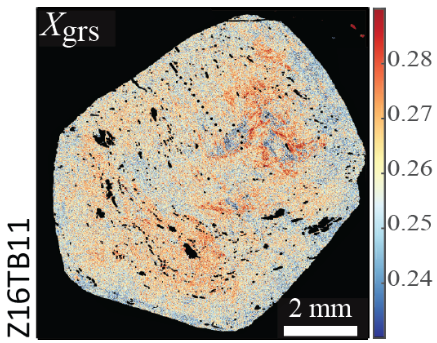
Mafic boudins



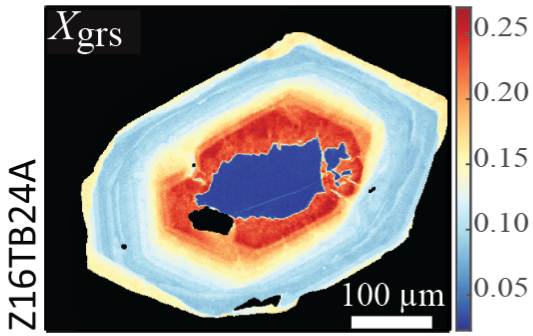


Mafic schist

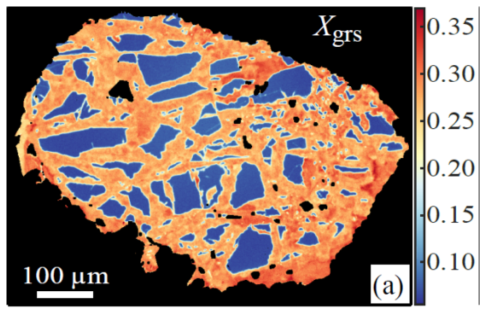




Chloritoid schist



Garnet schist



Bovay et al. 2021a, JMG, 10.1111/JMG.12623

Garnet age

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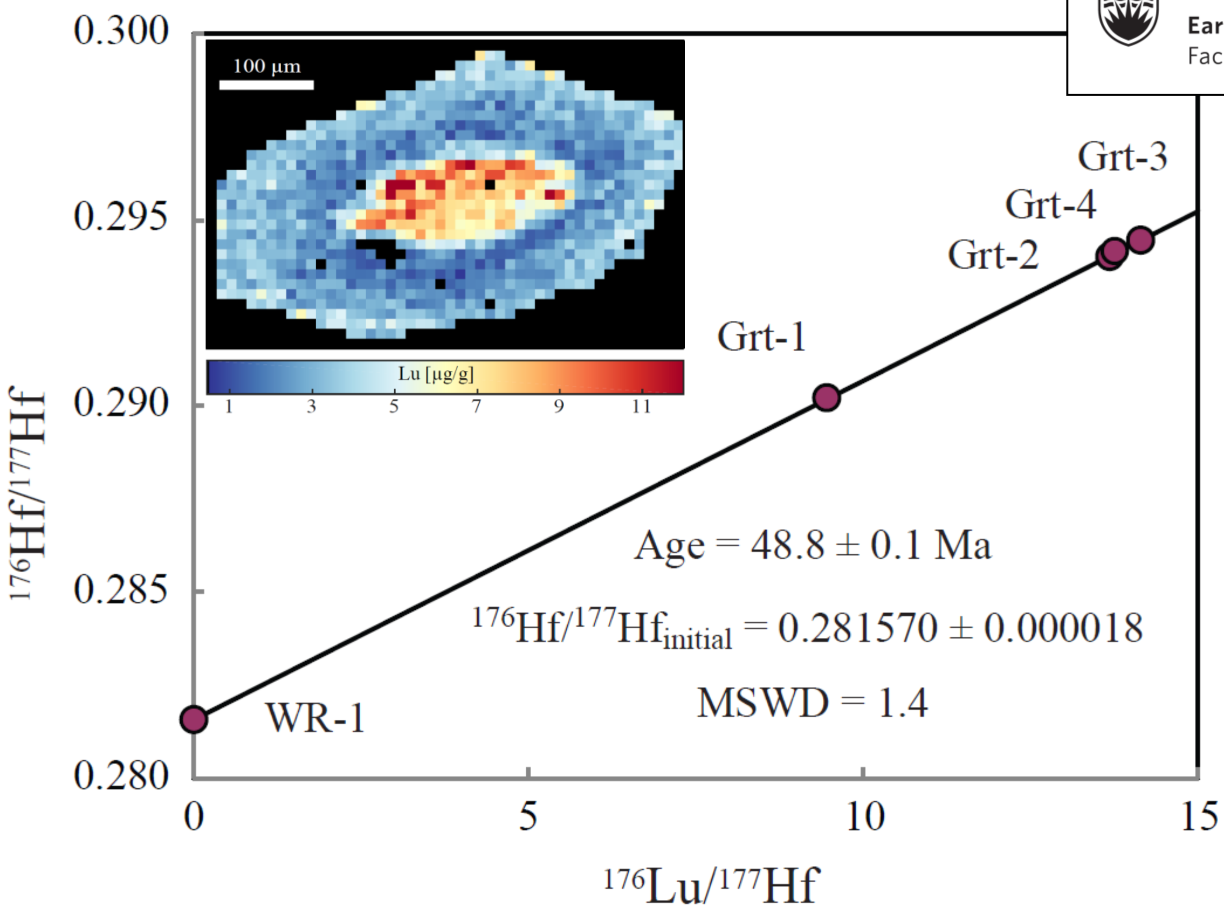
THE UNIVERSITY OF BRITISH COLUMBIA
Earth, Ocean and Atmospheric Sciences
Faculty of Science

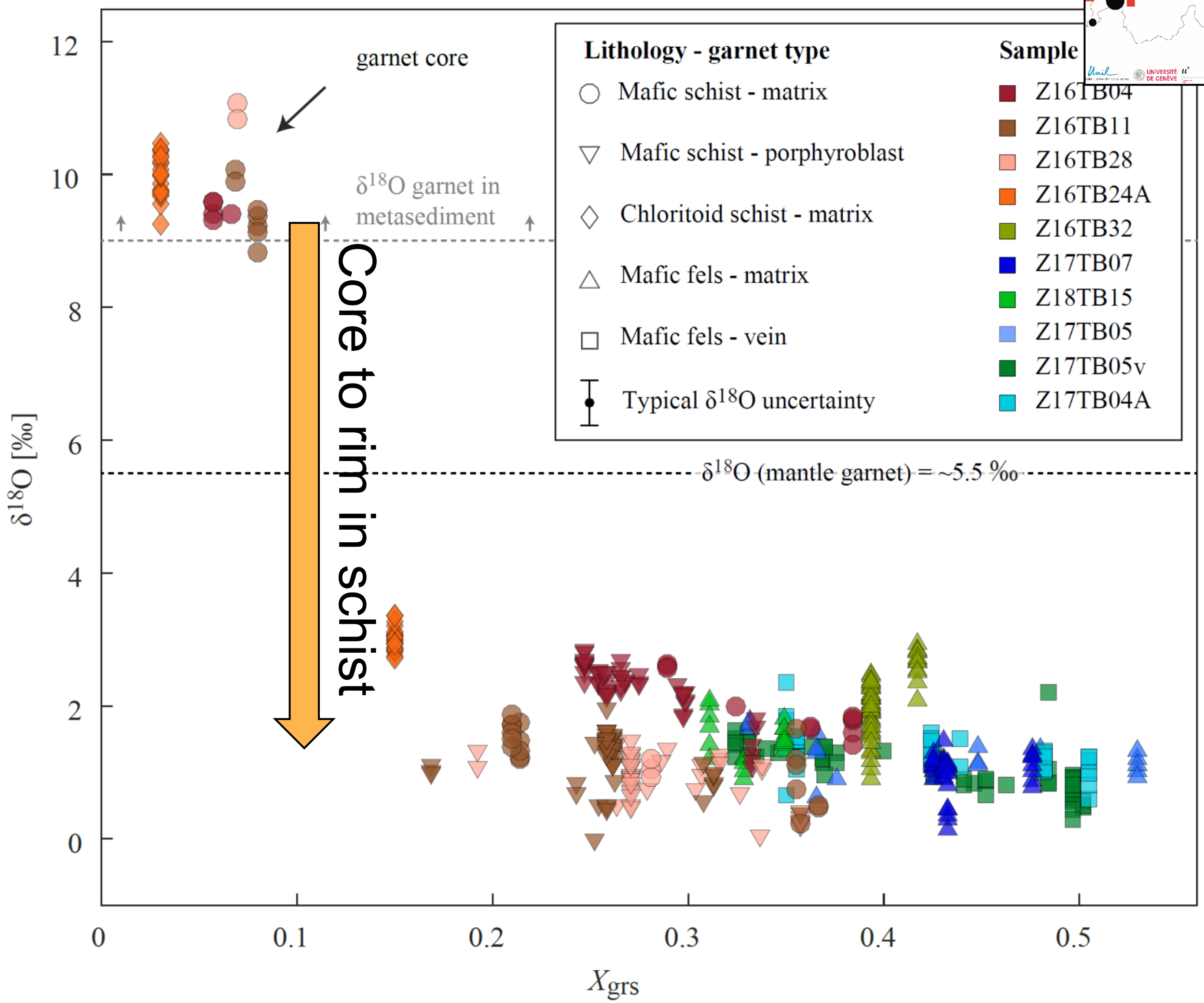
with Matthijs Smit

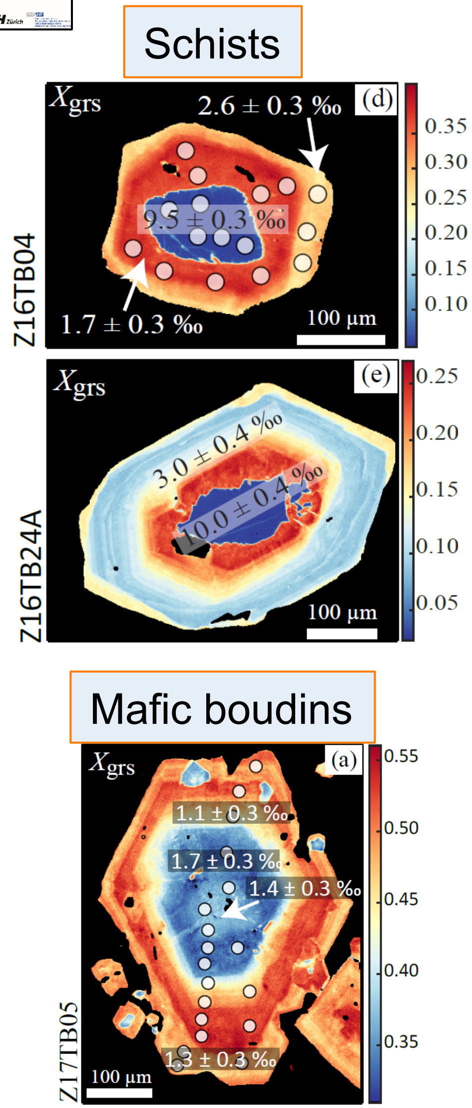


Monometamorphic Alpine evolution

Bovay et al. 2021a, JMG, 10.1111/JMG.12623

Garnet oxygen composition

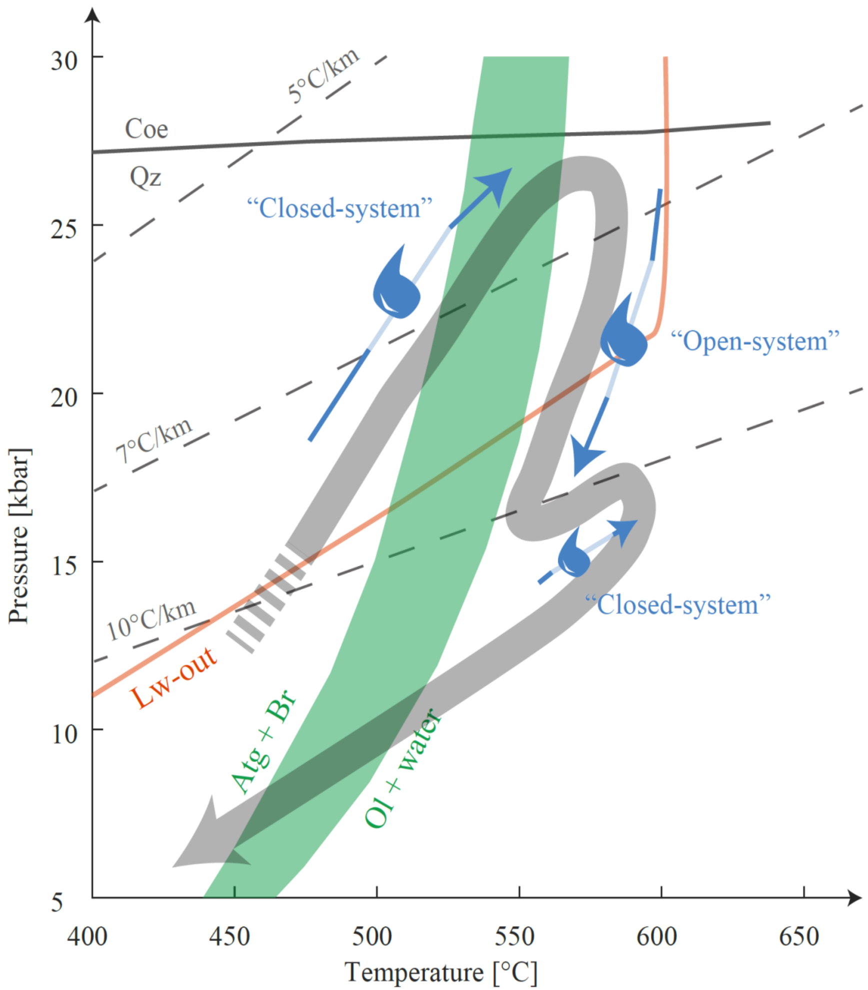




=> Open system behavior with incoming external fluids at high pressure over the entire unit

Bovay et al. 2021b, CMP, 10.1007/s00410-021-01806-4

Fluid modelling



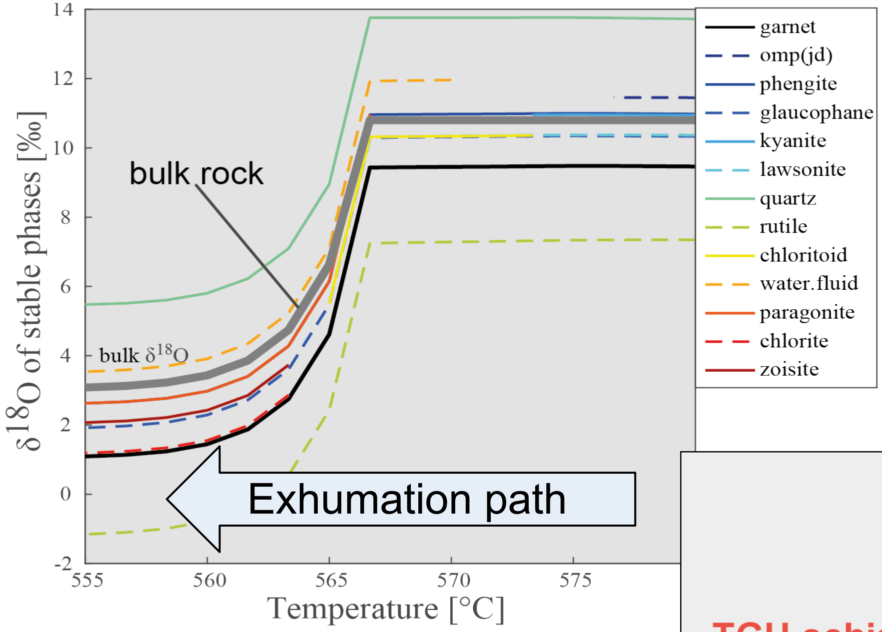
Garnet $\delta^{18}O$ 1 ‰ at 580 °C
=> H_2O ≤ 3.5 ‰

Lawsonite breakdown in mafic rocks ~ 2 wt% H_2O

Brucite + antigorite reaction in serpentinites = 3–7 wt% H_2O

Fluid modelling

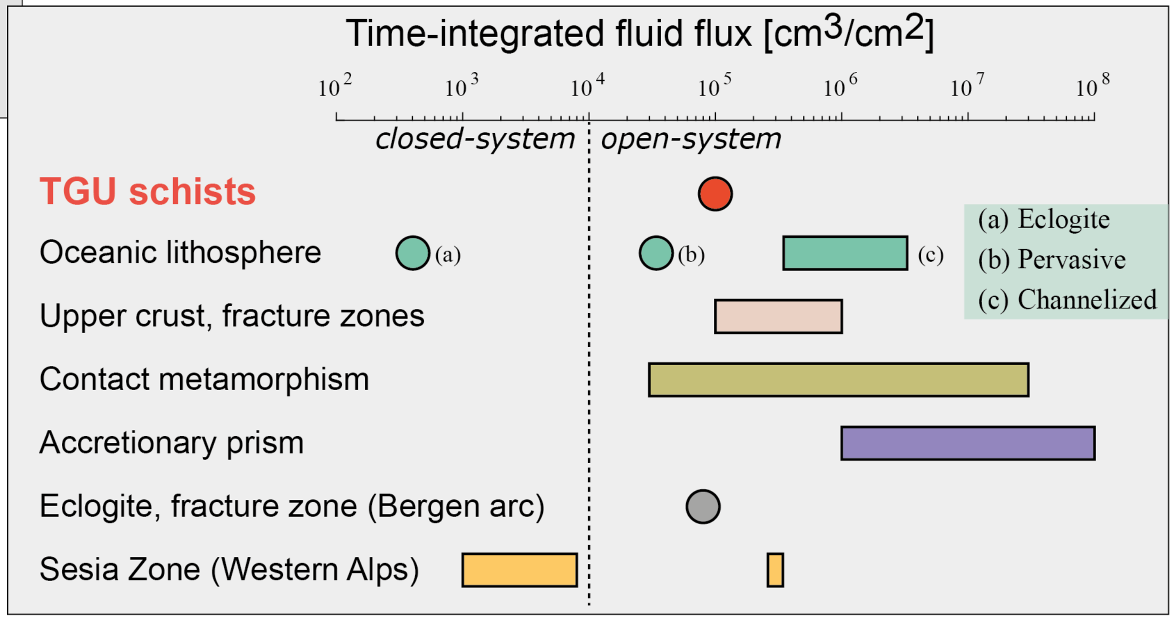
Using P-TLOOP (Vho et al. 2020)



Garnet $\delta^{18}O$ 1 ‰ at 580 °C
=> $H_2O \leq 3.5$ ‰

time integrated

Bulk rock $\delta^{18}O$ shift from 11 to 3 ‰
=> H_2O flux 1.1×10^5 cm^3/cm^2



Modified from Zack and John, 2007

Data from Zack and John 2007, Ferry and Gerdes 1998, Ague 2003, Philippot and Rumble 2000, Konrad-Schmolke et al. 2011, Vho et al. 2020

Fluid modelling

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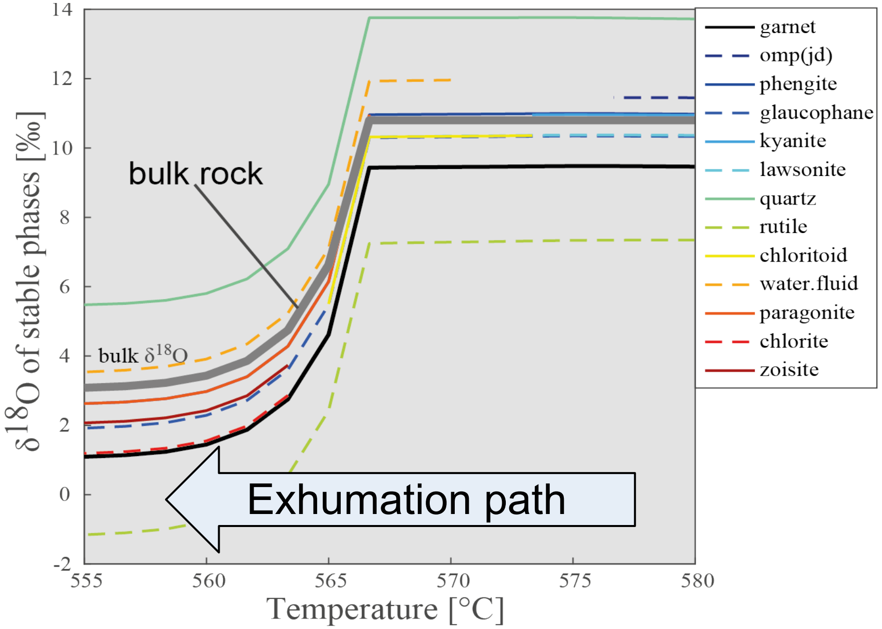
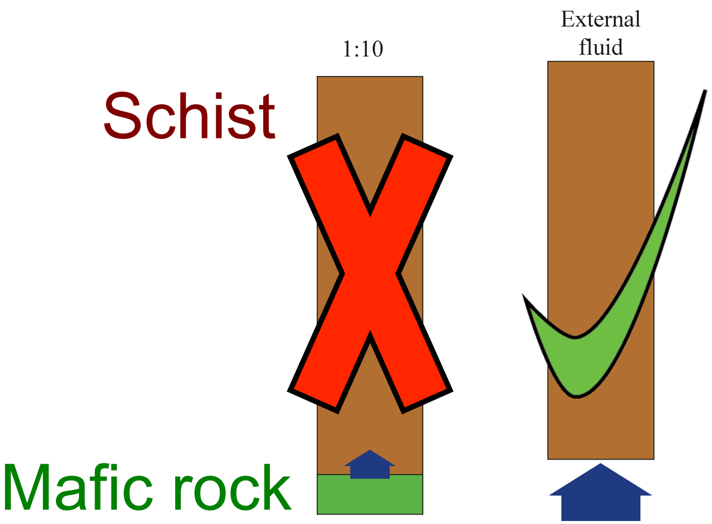
Using P-TLOOP (Vho et al. 2020)





Garnet $\delta^{18}O$ 1 ‰ at 580 °C
=> H_2O ≤ 3.5 ‰

time integrated

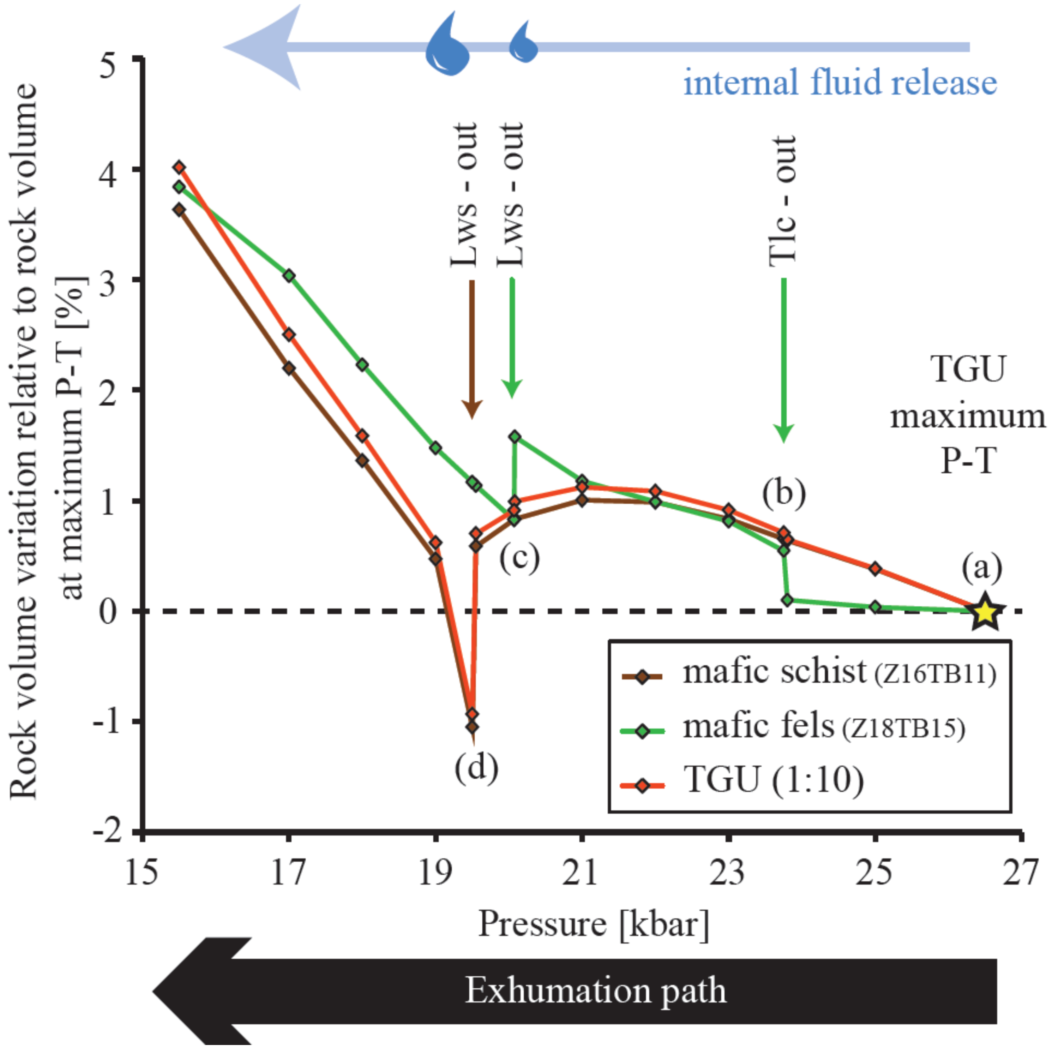
Bulk rock $\delta^{18}O$ shift from 11 to 3 ‰
=> H_2O flux 1.1 x 10^5 cm^3/cm^2

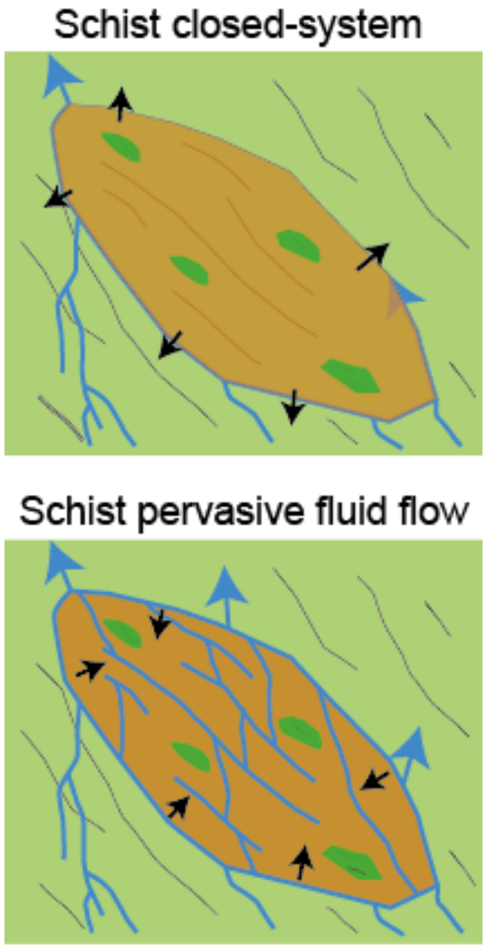
✗ Lawsonite breakdown in mafic rocks **cannot** produce

- water with low $\delta^{18}O$ ≤ 3.5 ‰
- such large amount of water

✔ Brucite+ antigorite reaction in serpentinites = 3–7 wt% H2O

Volume variation modelling

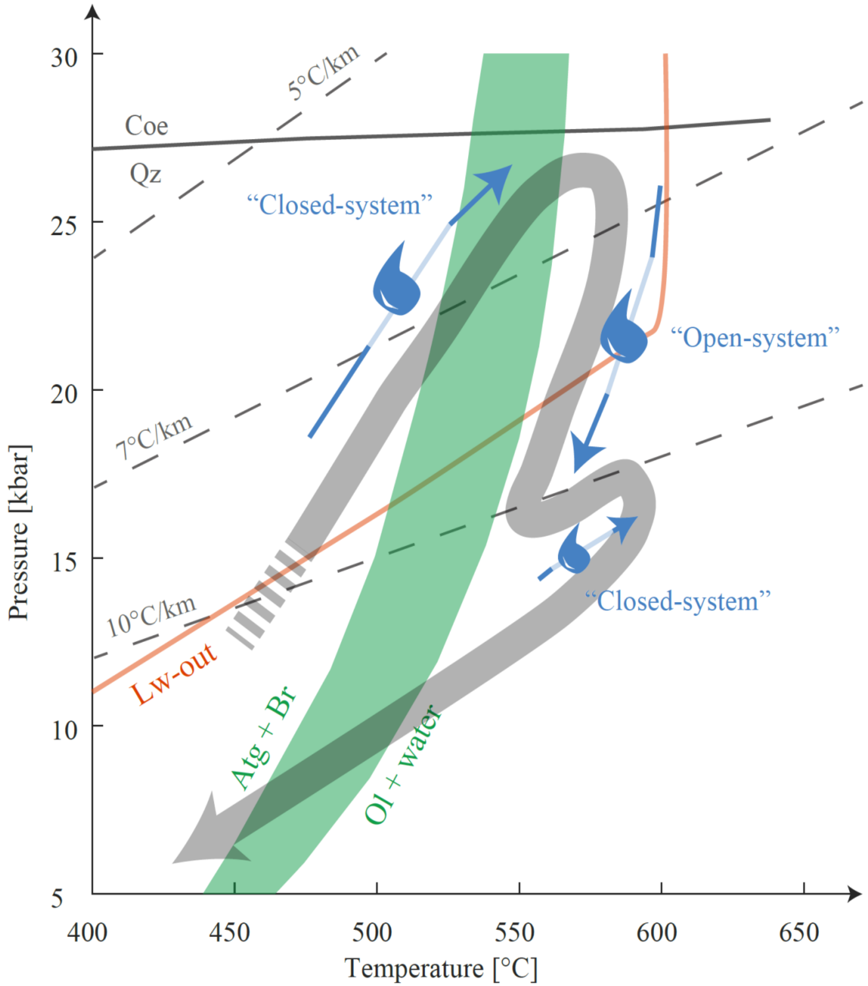




Bovay et al. 2021b, CMP, 10.1007/s00410-021-01806-4

Pervasive fluid flow in subducted crust

Modelling => H_2O flux at HP 1.1 x 10^5 cm^3/cm^2



- Elevated time-integrated fluid fluxes over the entire unit **requires pervasive fluid flow**

Trigger: transient rock volume variations caused by lawsonite breakdown

Fluid source: surrounding serpentinite

Bovay et al. 2021b, CMP, 10.1007/s00410-021-01806-4