Defects, Diffusion, Deformation and Thermal Conductivity in the Lower Mantle and D''

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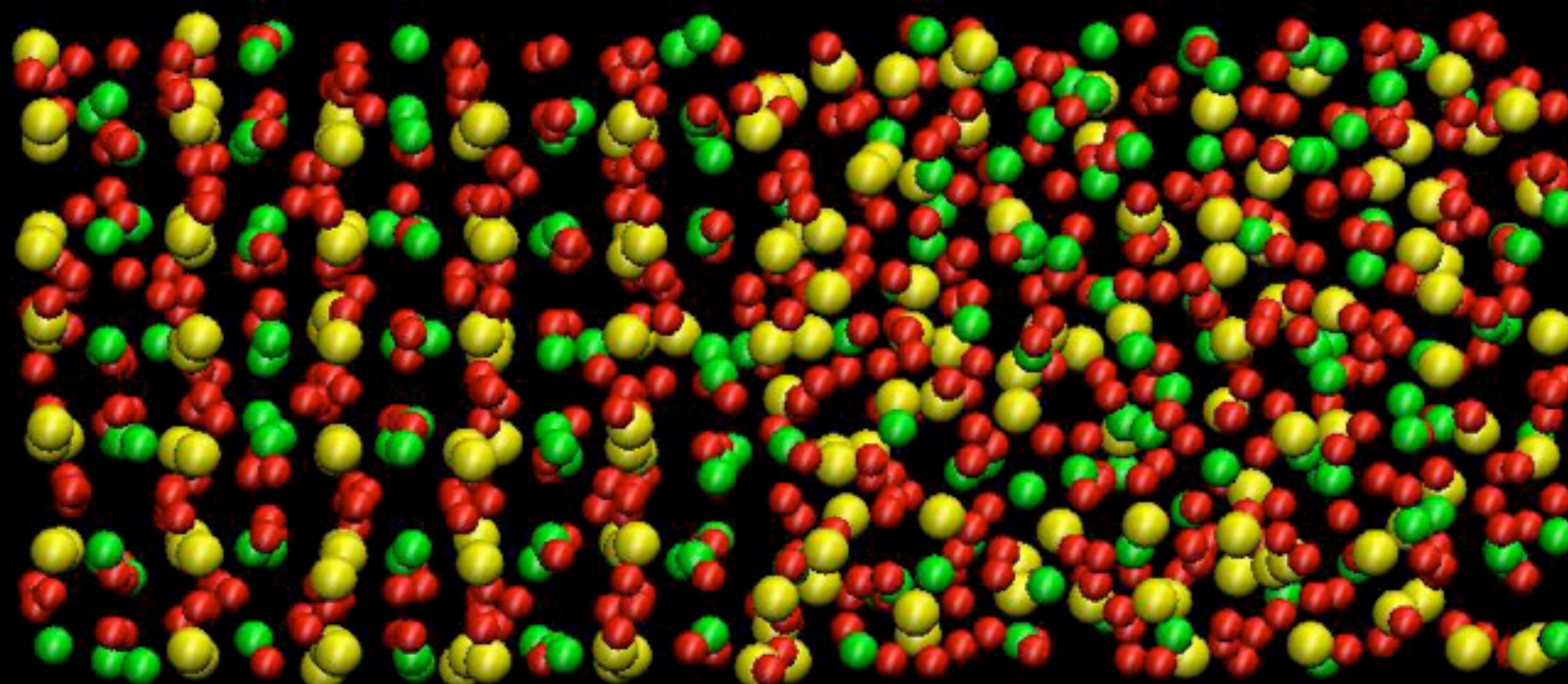
Thanks to: Michael Ammann, Simon Hunt,
James Wookey, Kai Wang, Andrew Walker and David Dobson

Defects and Diffusion is important:

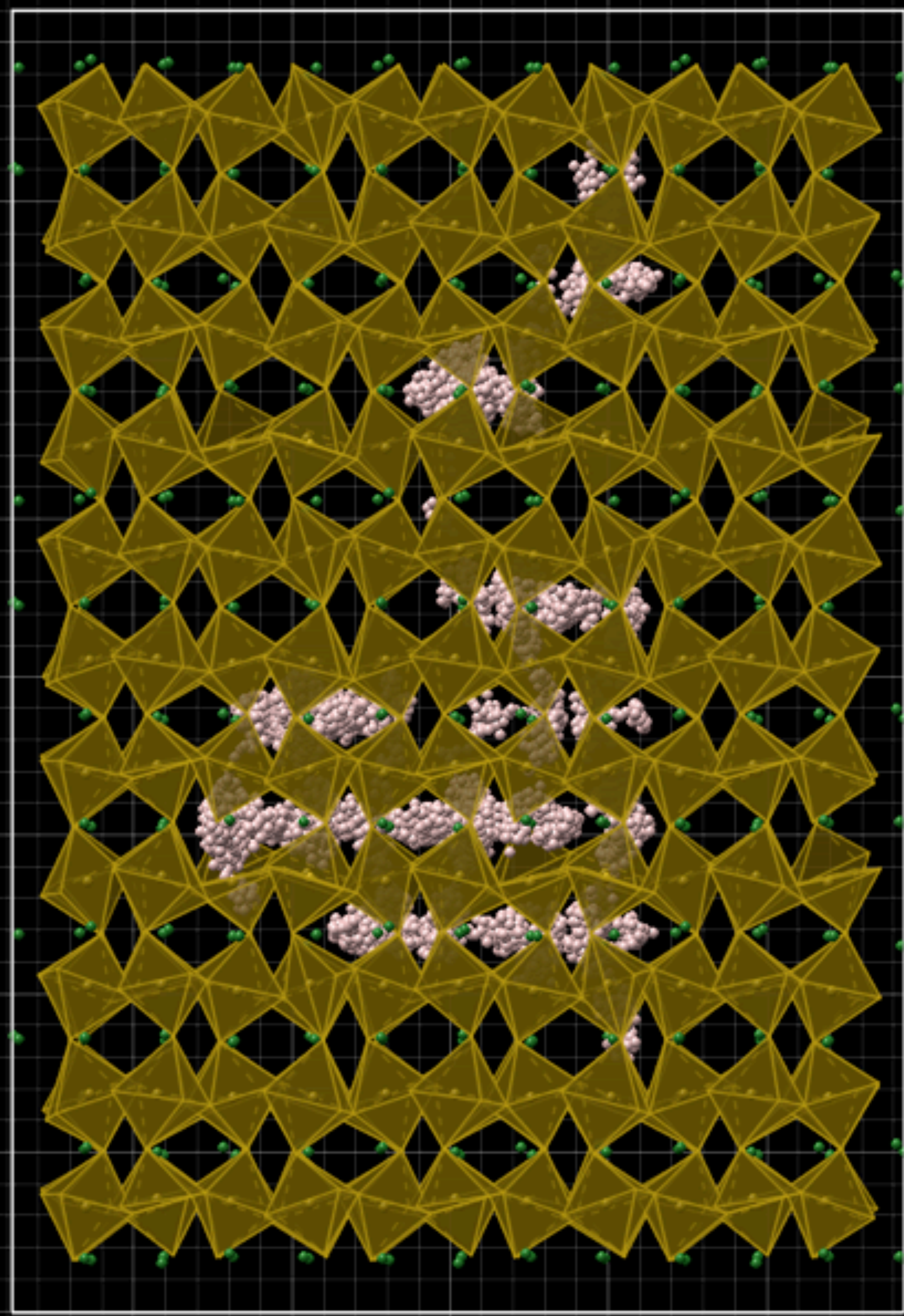
- Controls chemical exchange between crystalline, melt and fluid phases
- Degree of composition zoning in minerals
- Kinetics of phase transitions
- Rate at which minerals grow and their grain sizes
- Has a central role in controlling rheology **(Deformation)**

- High P & T experiments on diffusion are hard.
- So our approach is to use a theoretical approach (ab initio or first principles).



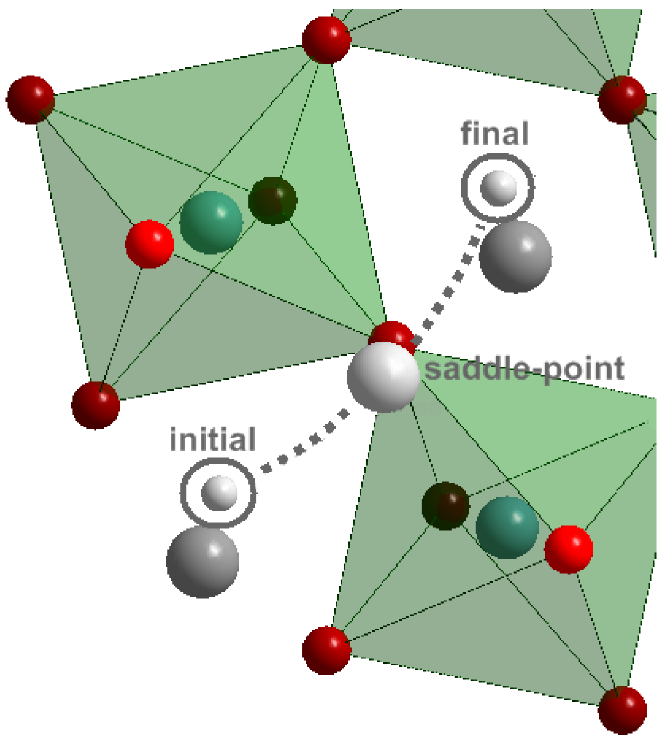
Forces are calculated either from “First principles” - quantum mechanics - or from “empirical potentials”.

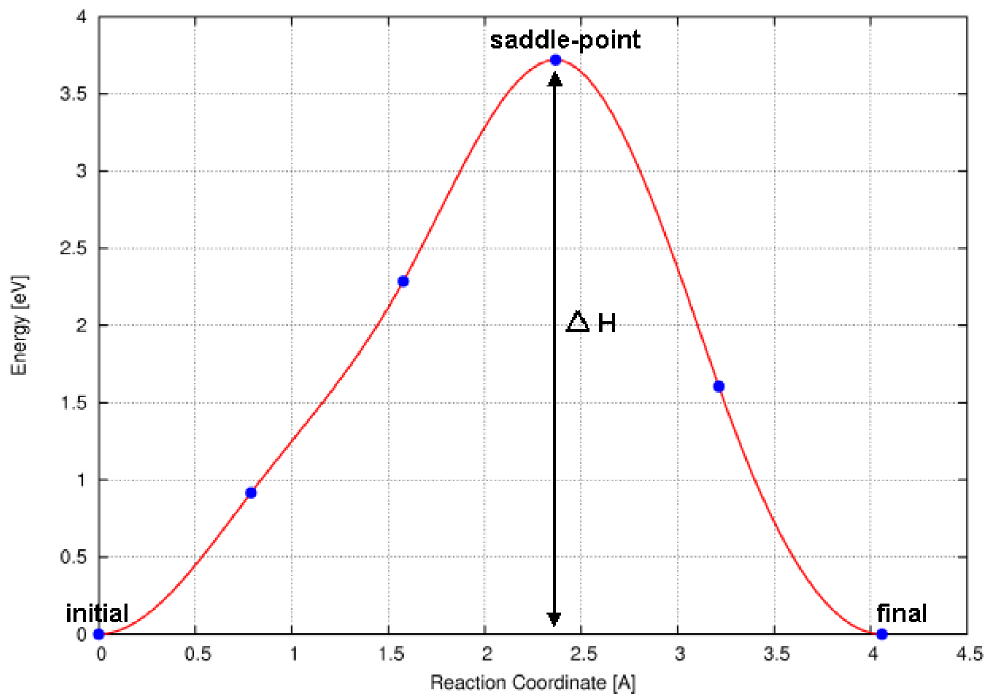
He diffusion in perovskite - the exception.



He diffusion in perovskite - the exception.

Self Diffusion: $$D_{sd} = AN_V \nu e^{\frac{\Delta S}{k}} e^{-\frac{\Delta H}{kT}}$$





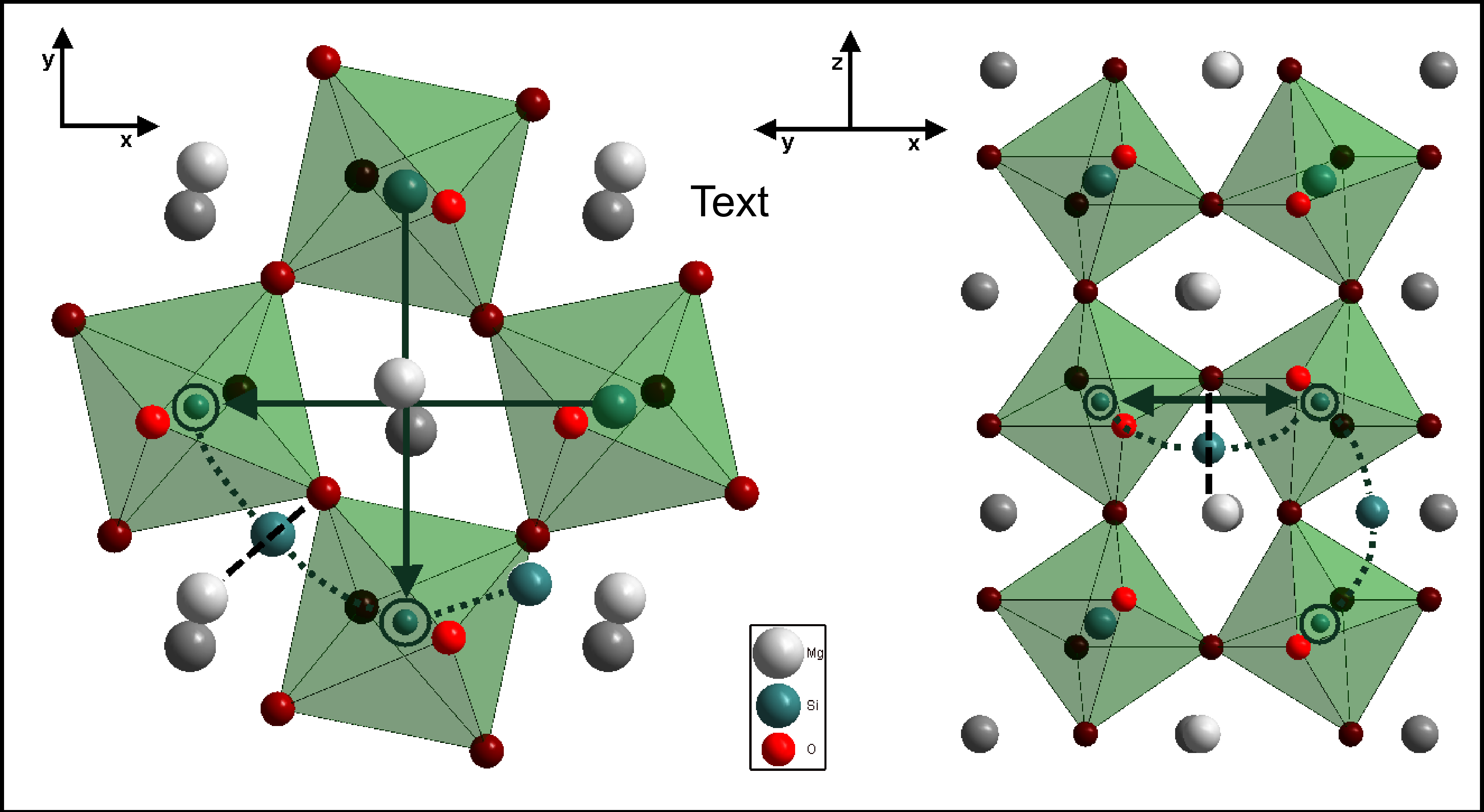
All energies and frequencies obtained from DFT calculations

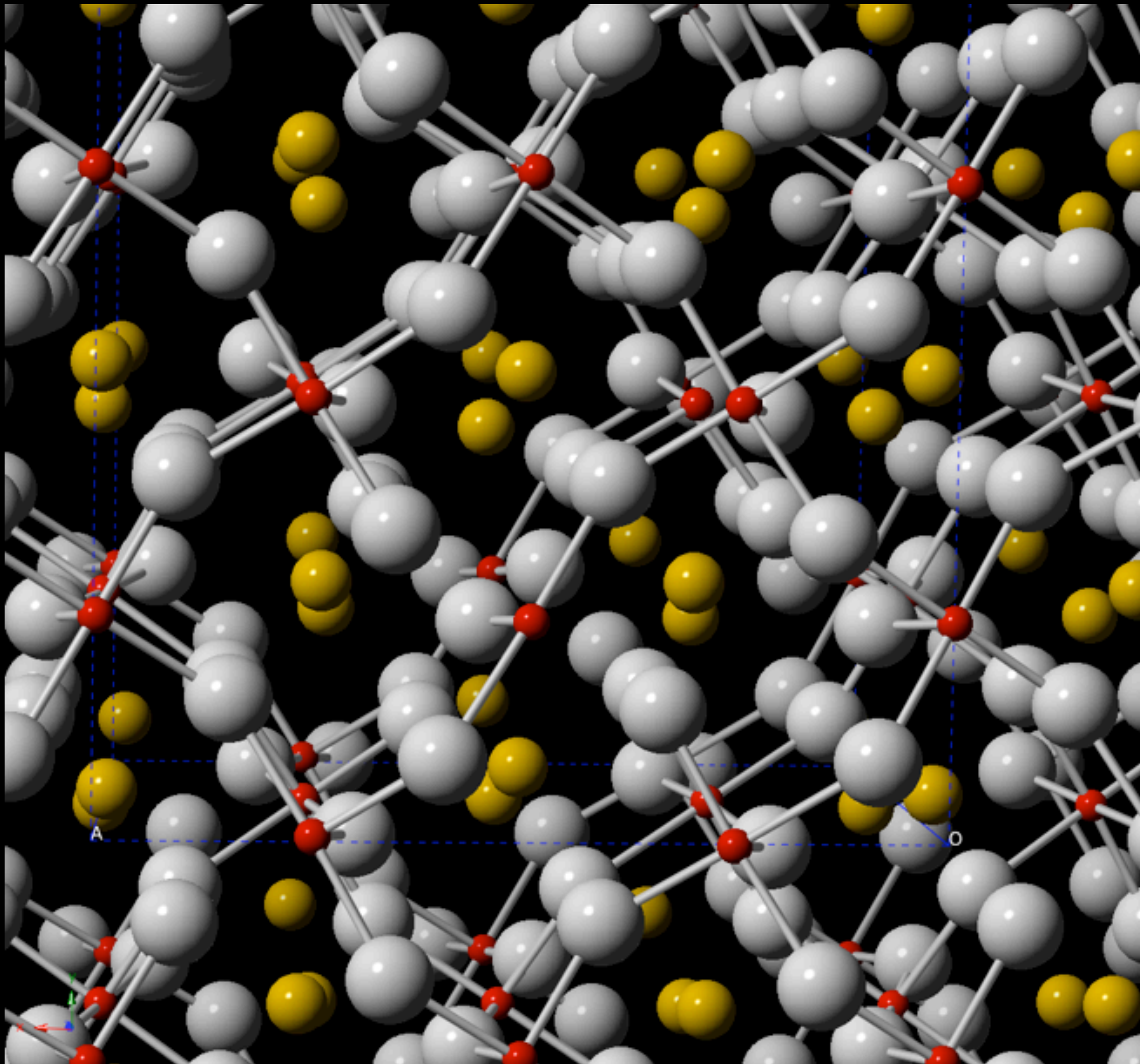
Migration enthalpy: $$\Delta H = E_{saddlepoint} - E_{initial}$$

Attempt frequency and migration entropy (Vineyard Theory)

$$\nu e^{\frac{\Delta S}{k}} = \frac{\prod_{n=1}^{N} f_i}{\prod_{n=1}^{N-1} f_i'}$$

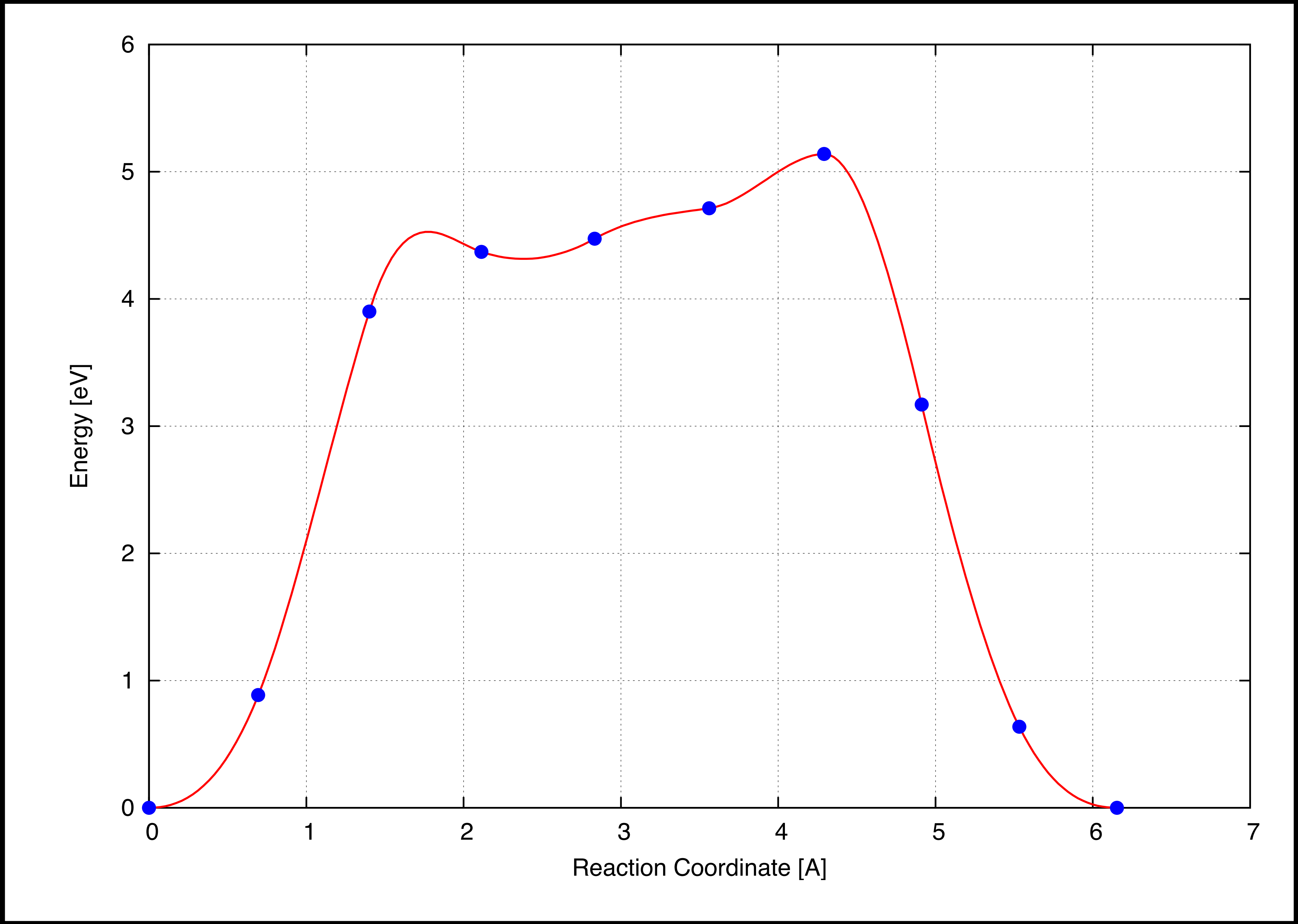
Theory: Wright & Price (1993) = 9.4 eV (empirical potentials)
Experiments: Yamazaki et al., (2000) = 3.6 eV
Theory: Karki and Khanduja (2007) = 9 eV (DFT)
Experiments: Dobson et al, (2008) = 3.7 eV





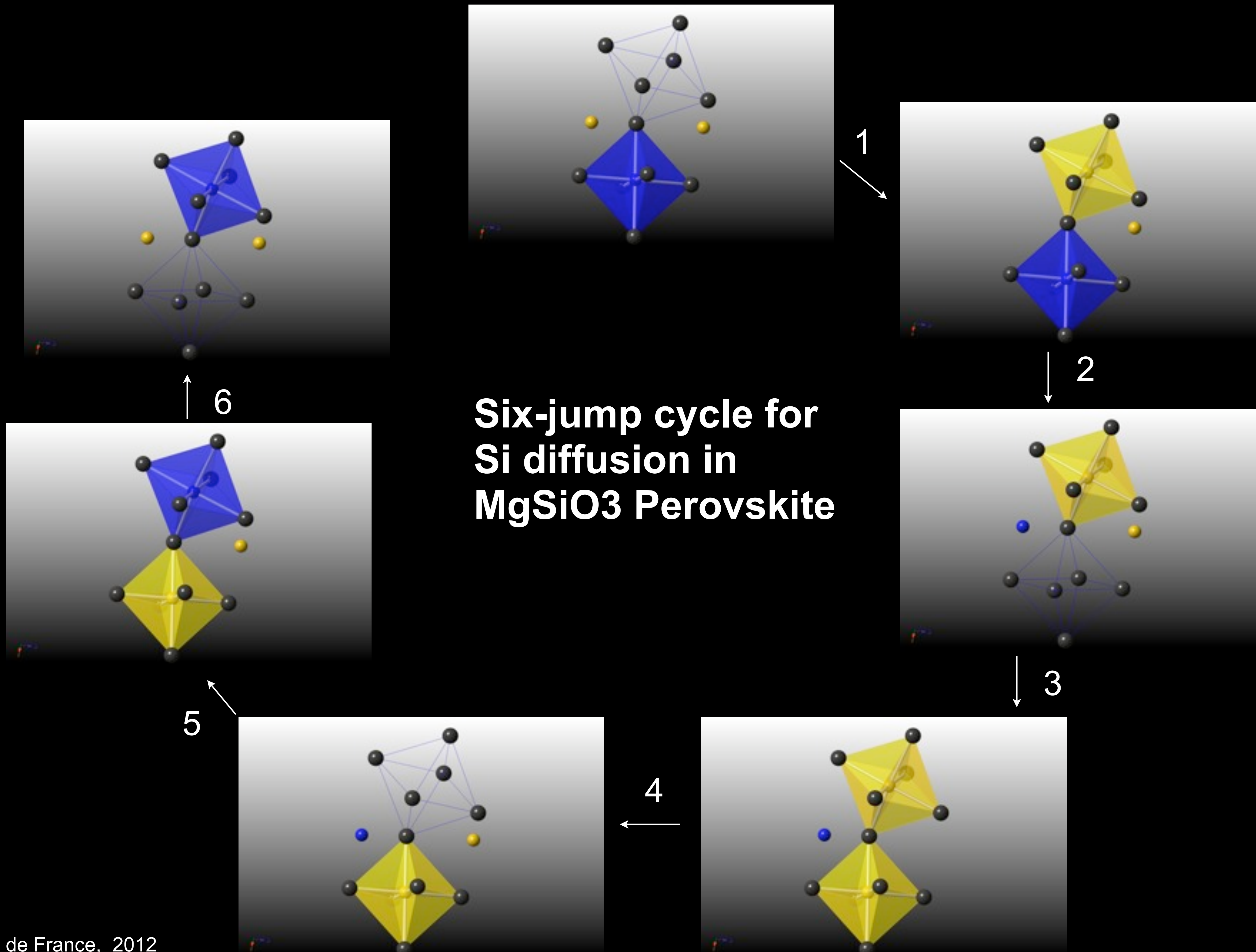
Si Diffusion in Perovskite

Si diffusion in MgSiO3 perovksite

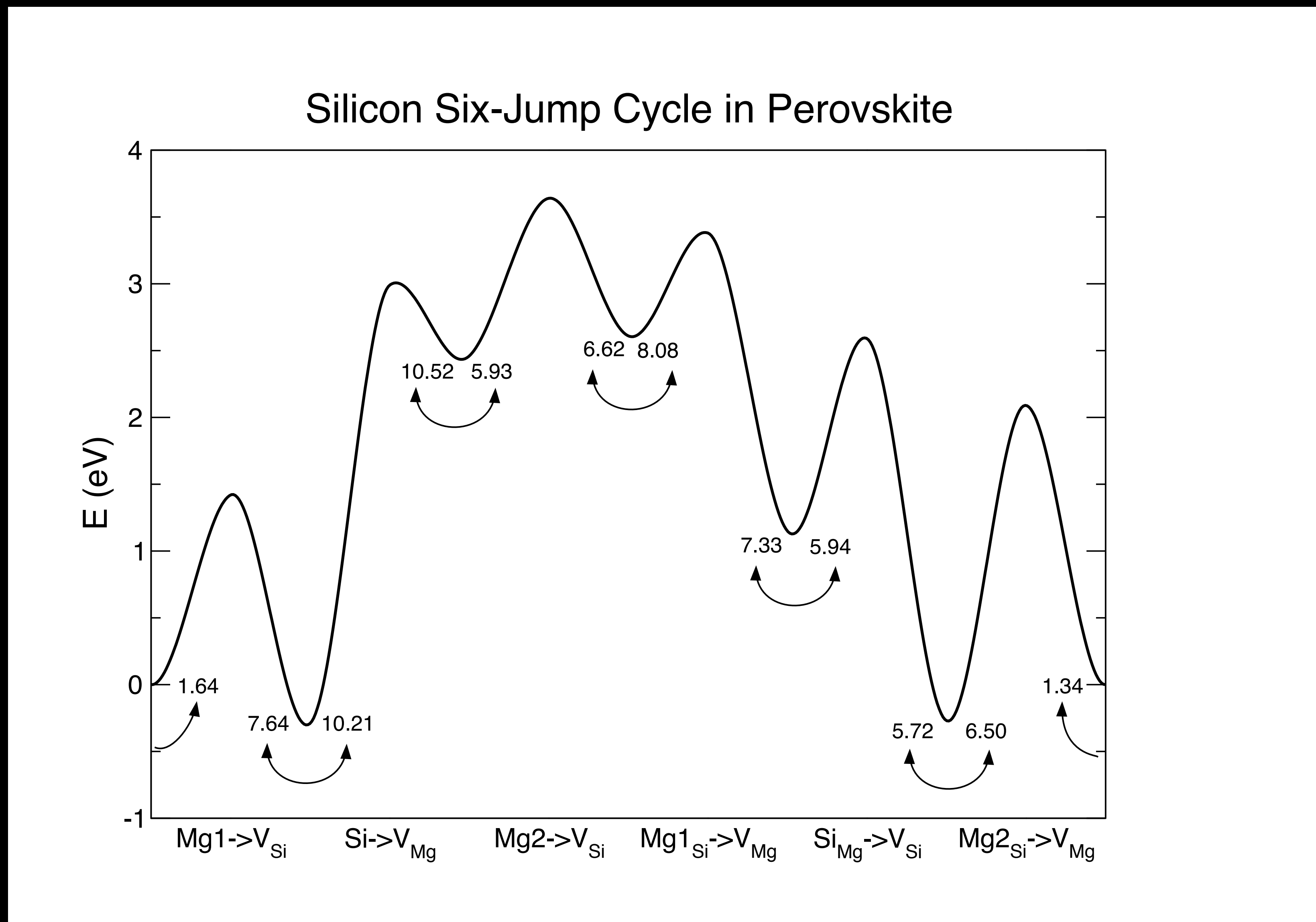


Agreement with experiment (3.6 eV) is better than previous estimates (9 eV) but still not great!

Six-jump cycle for Si diffusion in MgSiO3 Perovskite

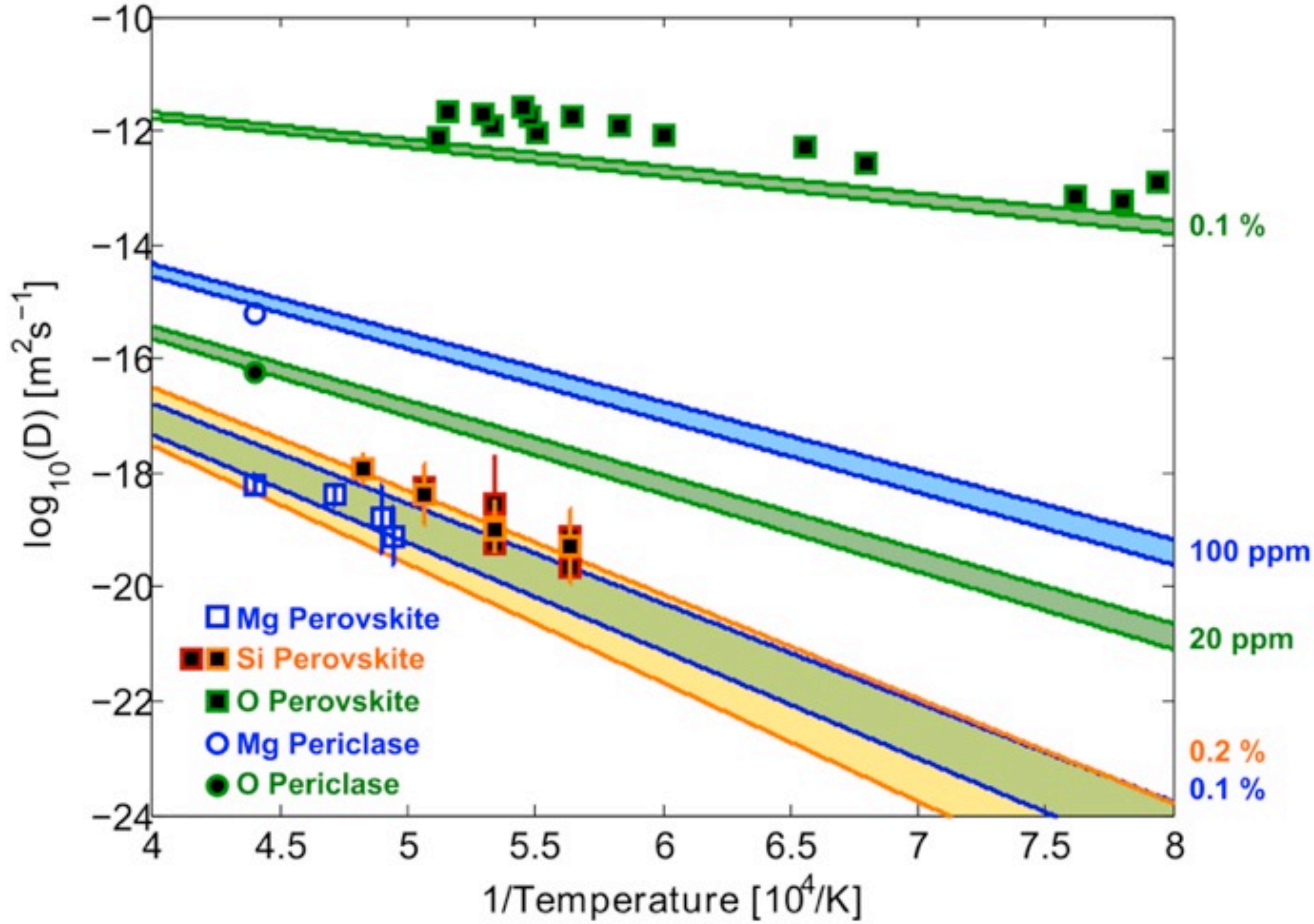


Si diffusion in perovksite does not seem to occur via a simple vacancy hoping mechanism



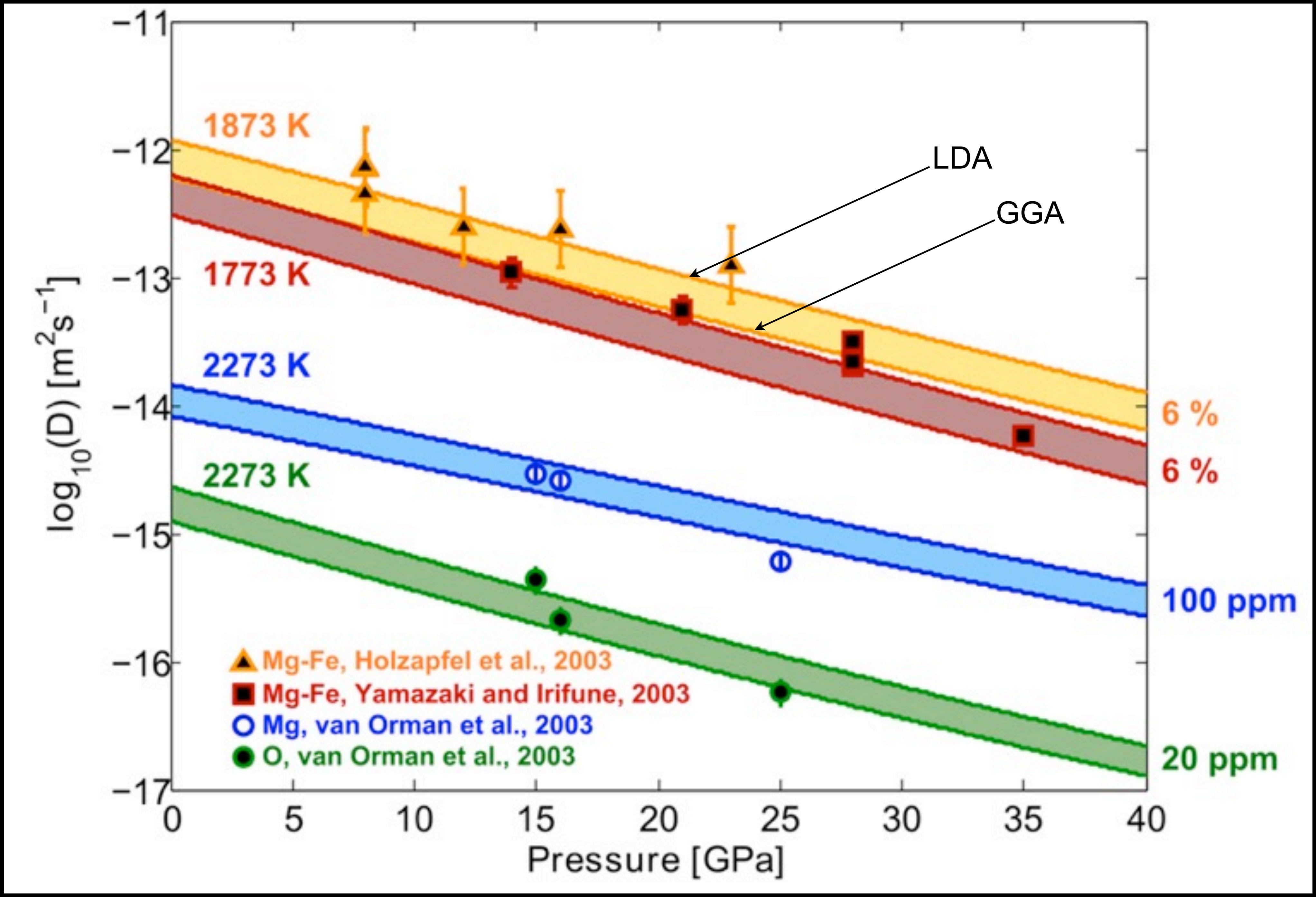
Apparent activation energy for the total cycle is 3.6 eV. This agrees well with 3.61 eV and 3.5 eV found by Dobson et al. (2008) and Yamazaki et al (2000).

PEROVSKITE DIFFUSION RATES



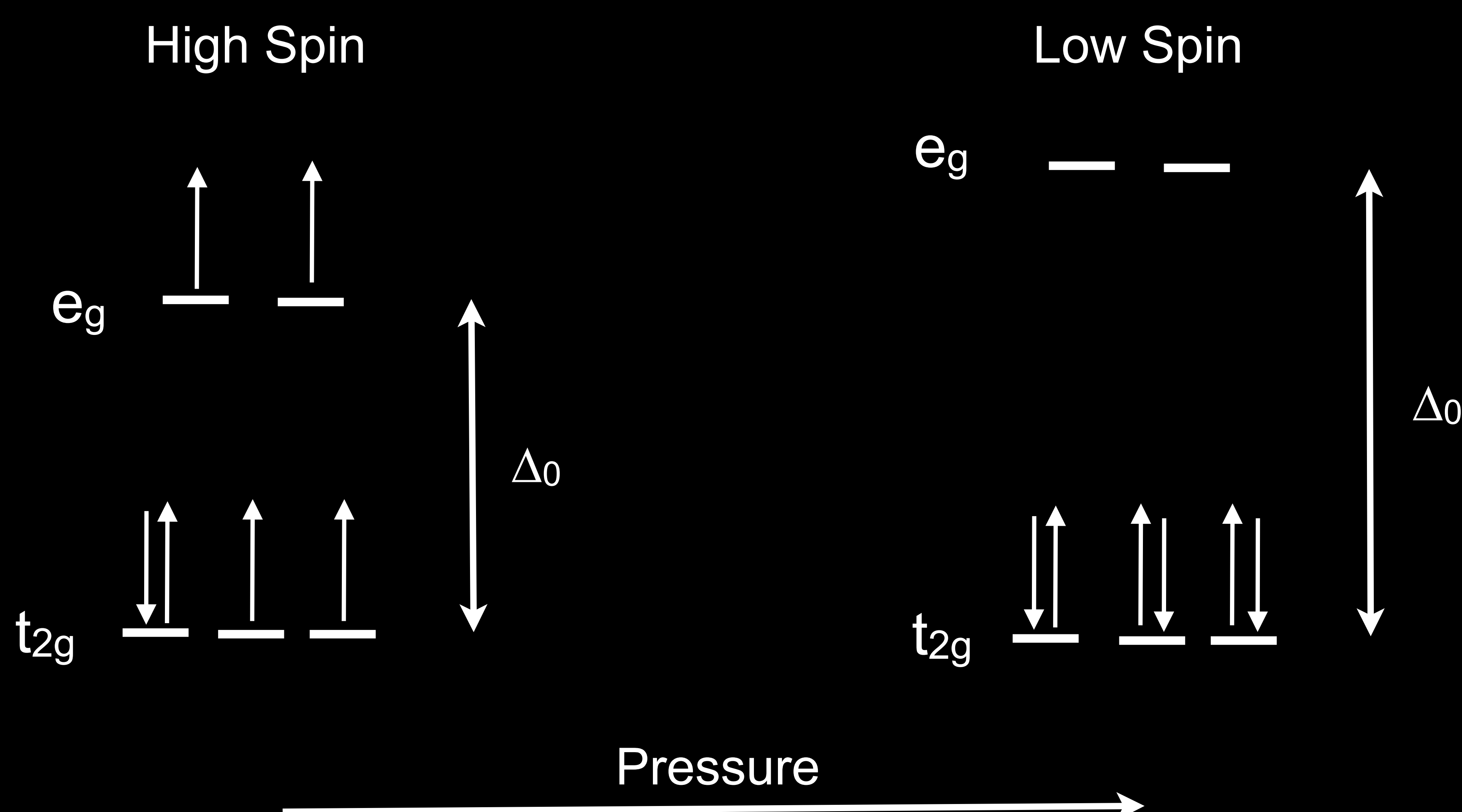
Periclase: *van Orman et al. (2003),*
Si Perovskite: *Dobson et al. (2008), Yamazaki et al. (2000)*
Mg Perovskite: *Holzapfel et al. (2005)*
O Perovskite: *Dobson (2003)*

Absolute Diffusion Rates in MgO

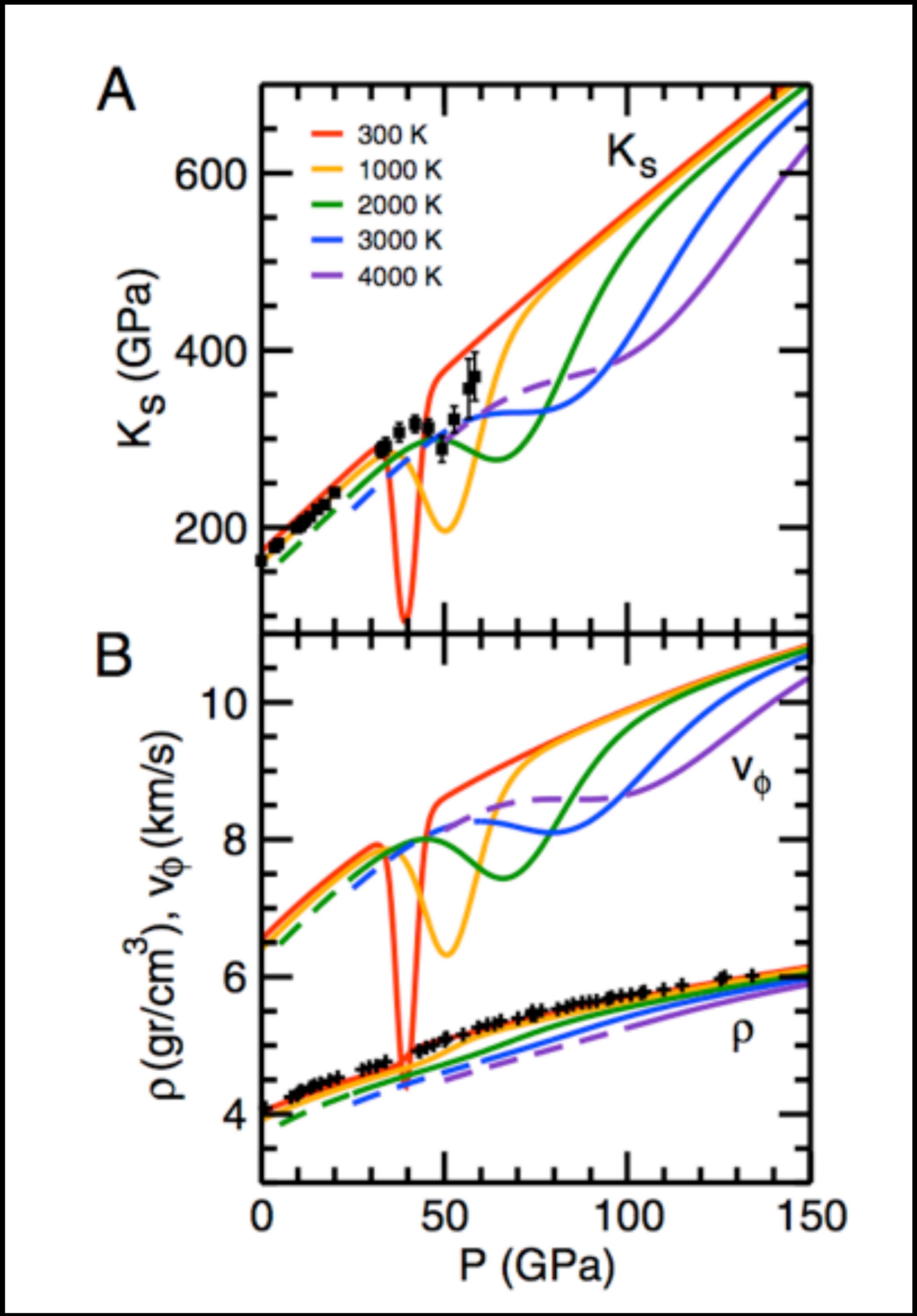


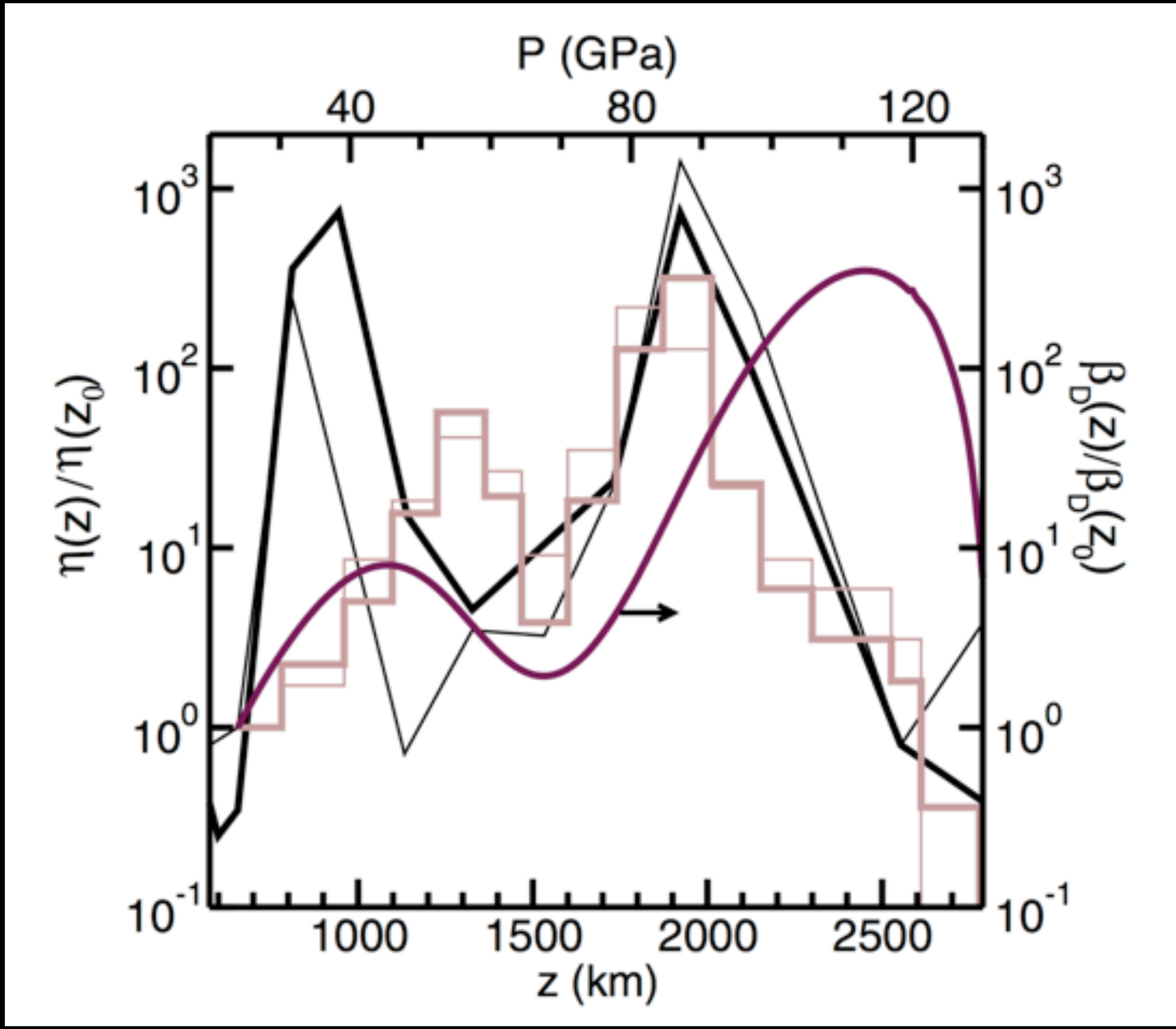
What about other components?
Fe^{2+}, Fe^{3+}, Al^{3+} etc.

And in particular the effect of spin transition in Fe.



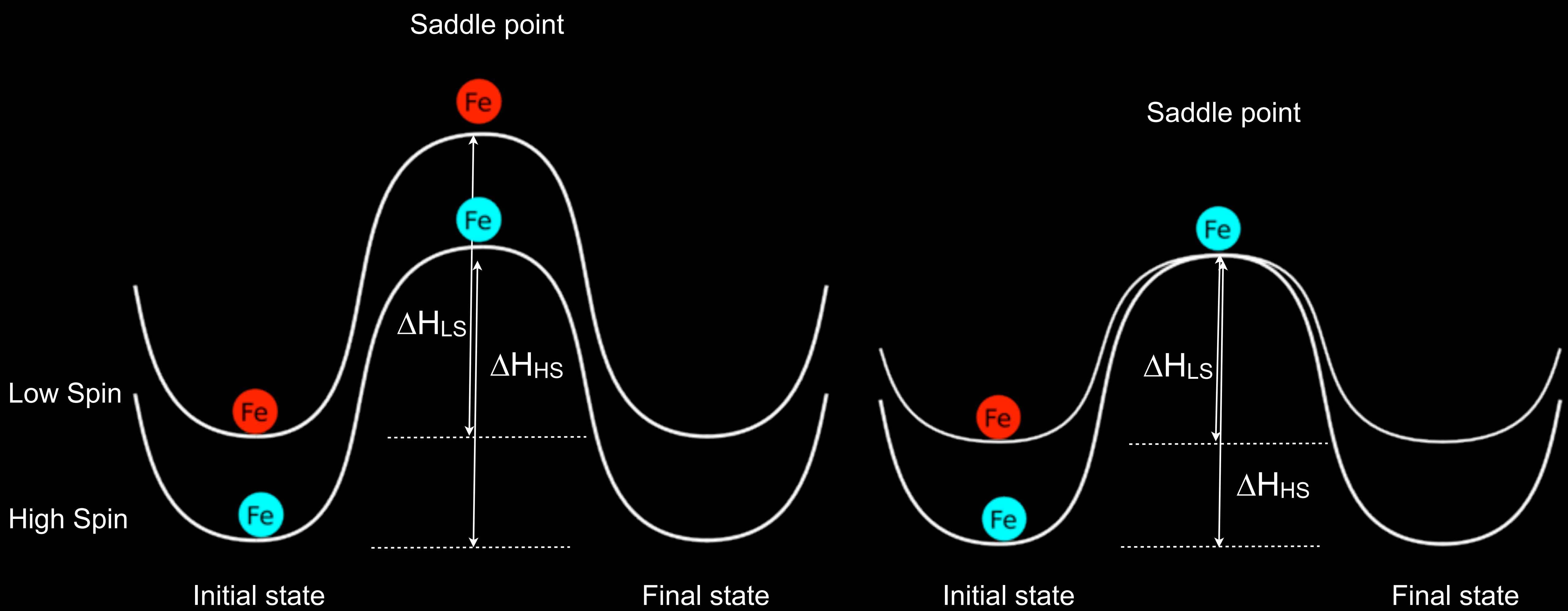
High - Low Spin Transition in Ferropericlase





Wentzcovitch et al. PNAS 2009

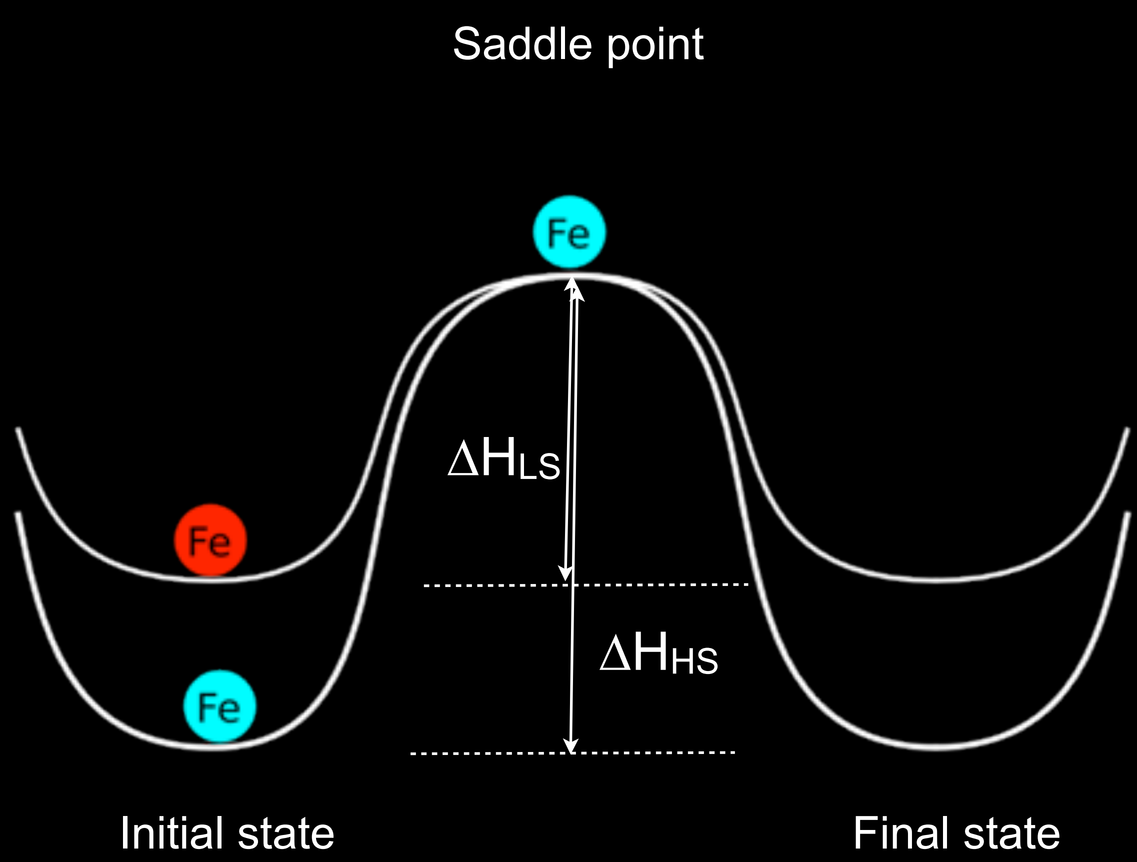
Low Pressure



$\Delta H_{LS} \sim \Delta H_{HS}$

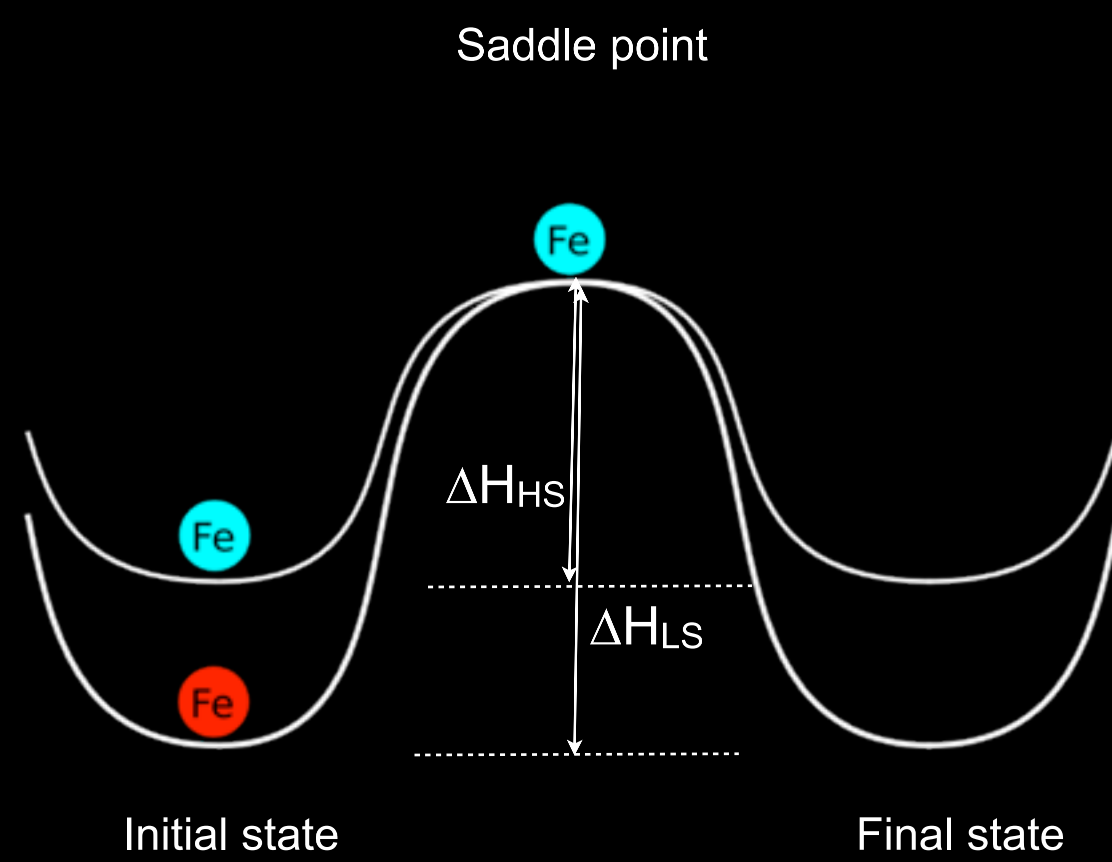
$\Delta H_{LS} < \Delta H_{HS}$

Low Pressure

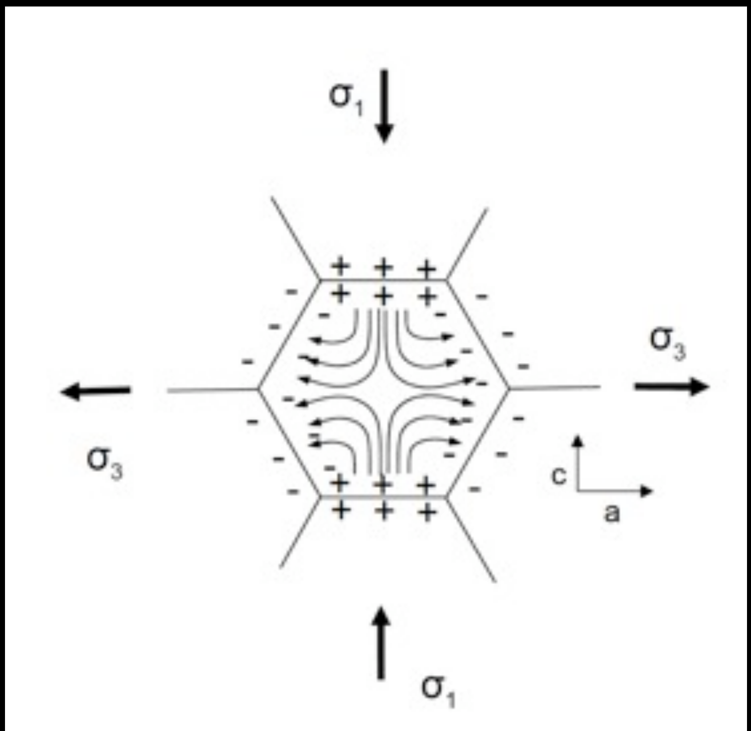


$\Delta H_{LS} < \Delta H_{HS}$

High Pressure

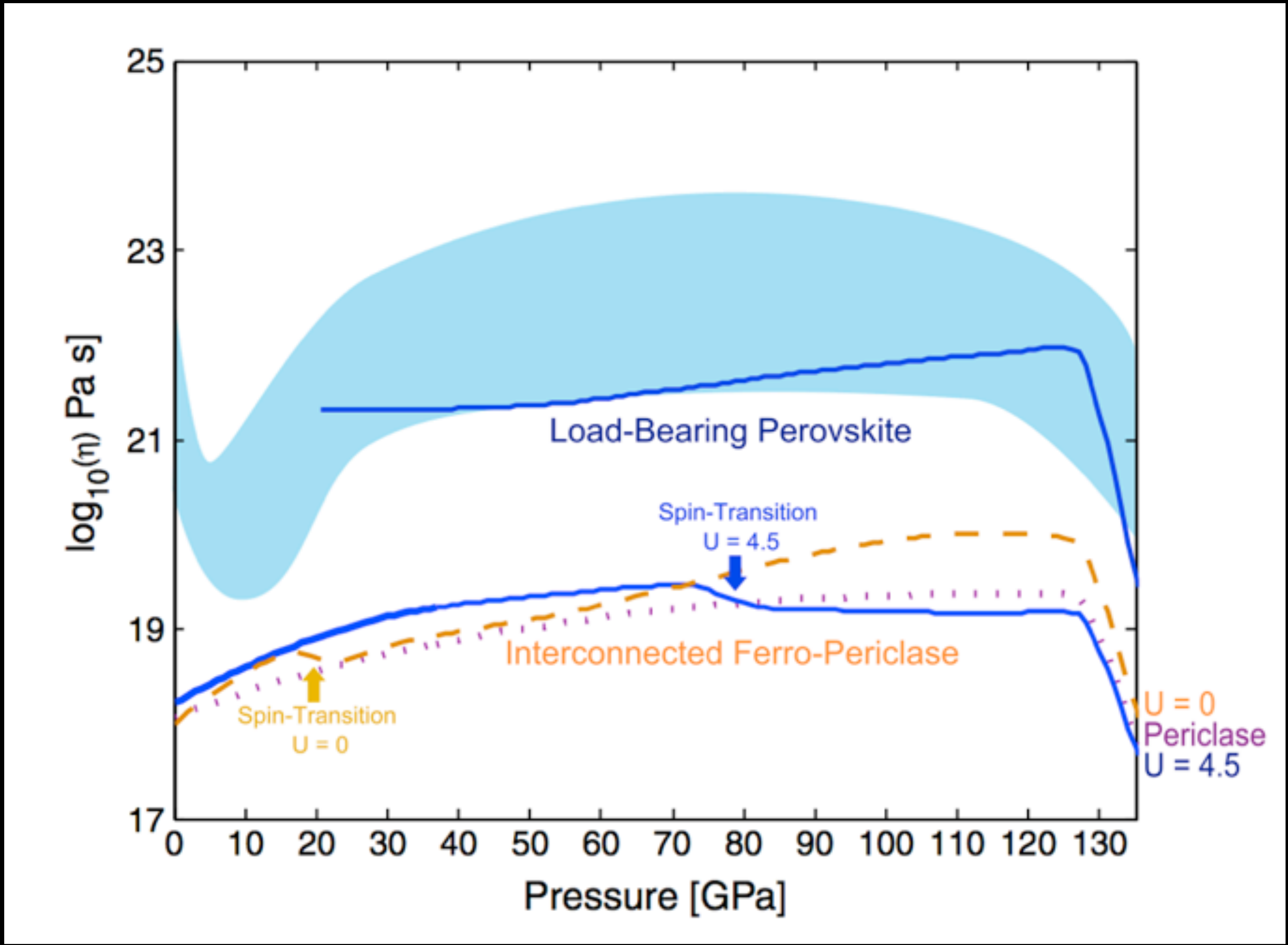


$\Delta H_{LS} > \Delta H_{HS}$

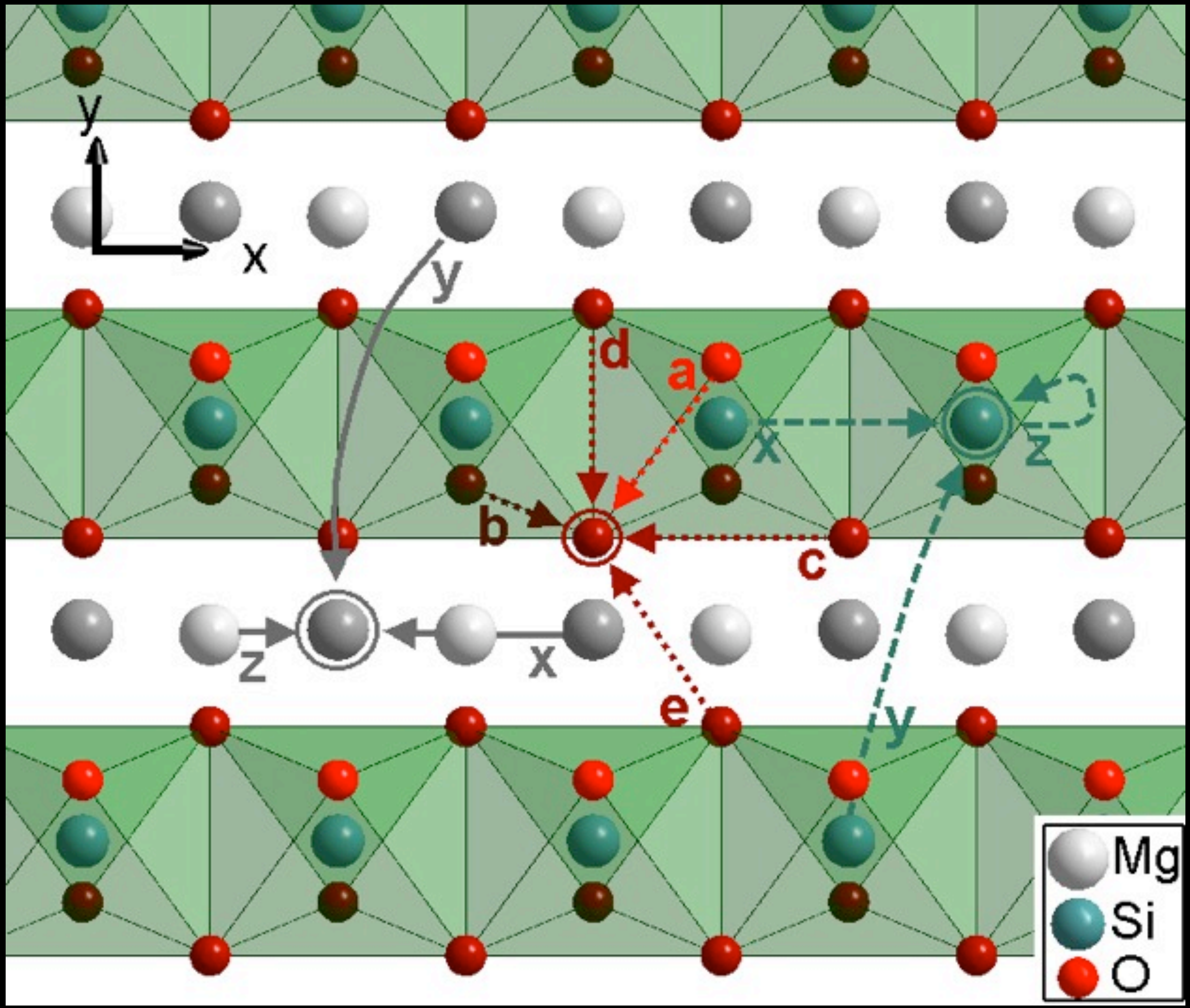


$$\eta = \frac{\sigma}{\dot{\epsilon}} = \frac{G^2 kT}{\alpha D \Omega}$$

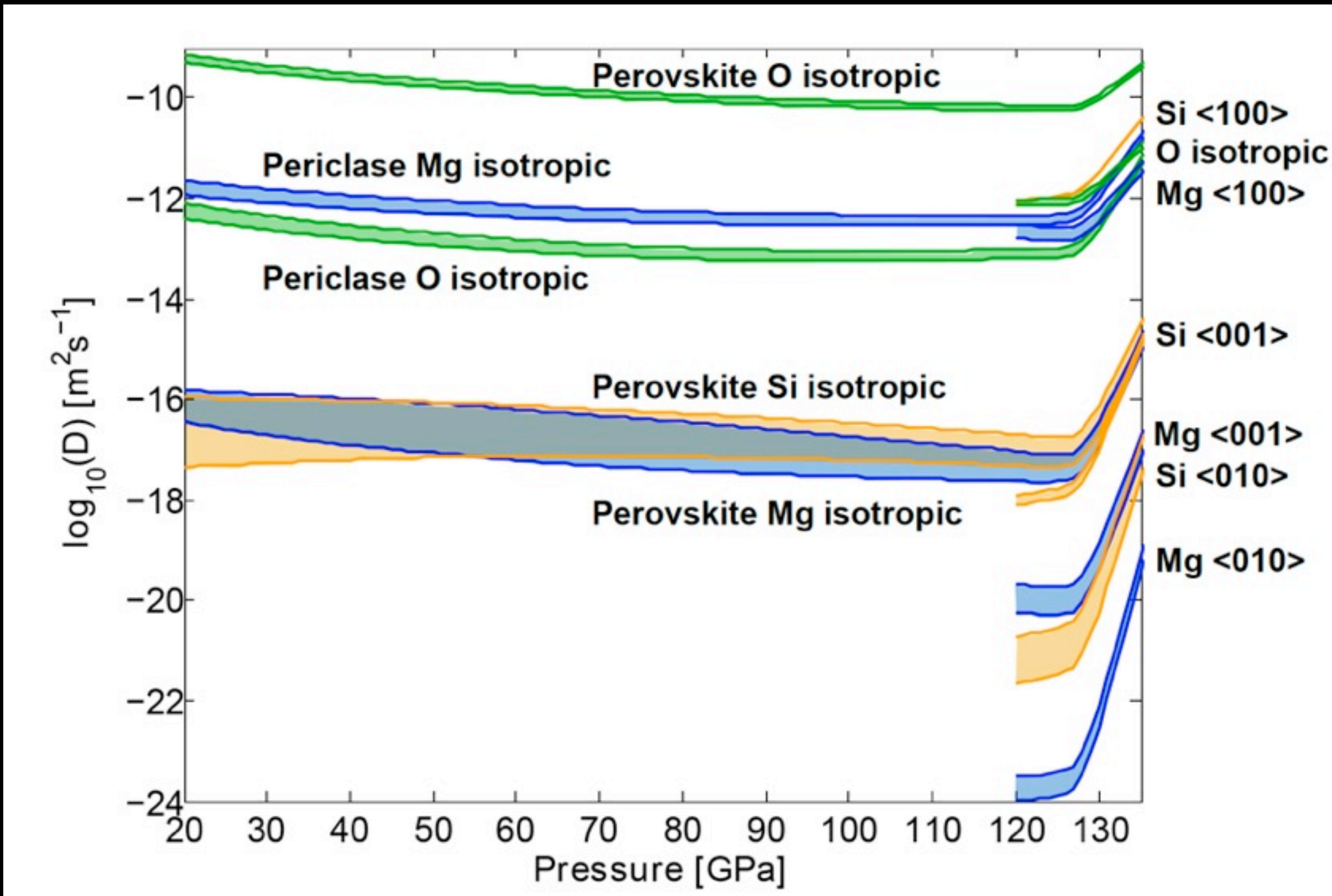
(Nabbaro-Herring Creep)



Diffusion in post-perovskite

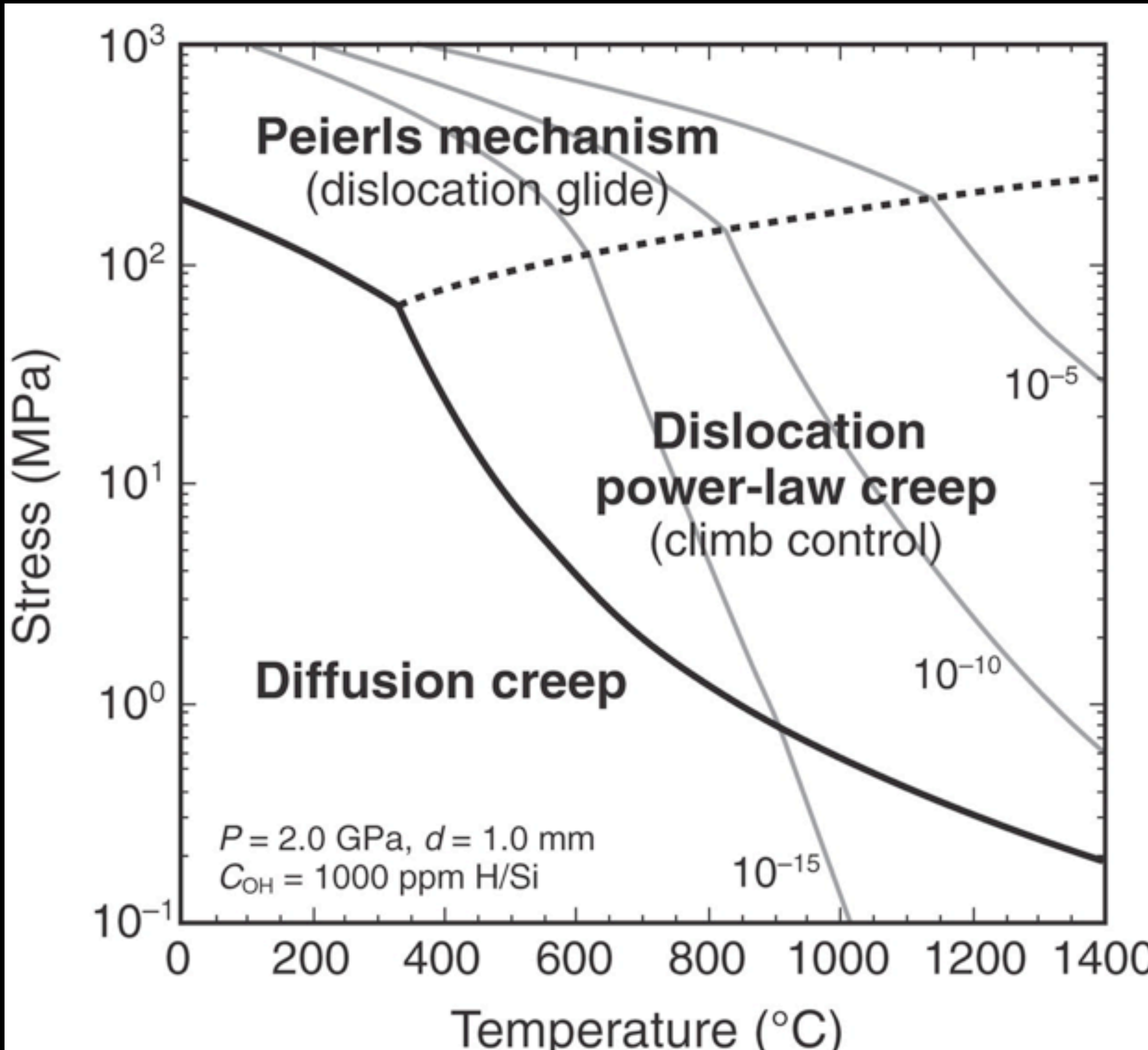


Diffusion in post-perovskite is extremely anisotropic.



Si and Mg diffusion in the <100> direction is very fast

Deformation Map for Olivine



Katayama, Geology (2012)

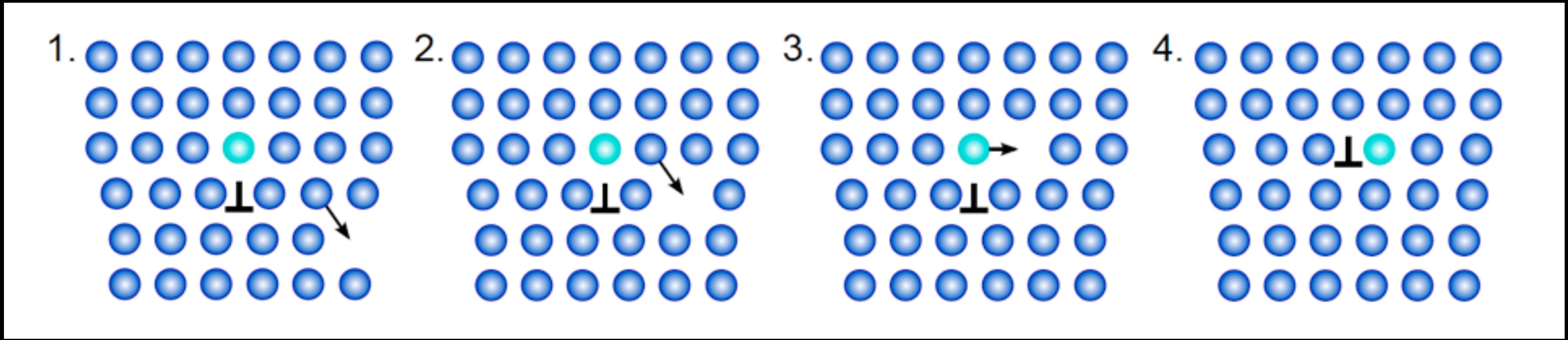
Don't know deformation map for PPV, but ....

If diffusion creep, PPV could be several orders of magnitude more viscous that PV.

If dislocation creep, PPV could be up to four orders of magnitude weaker than PV - if climb controlled.

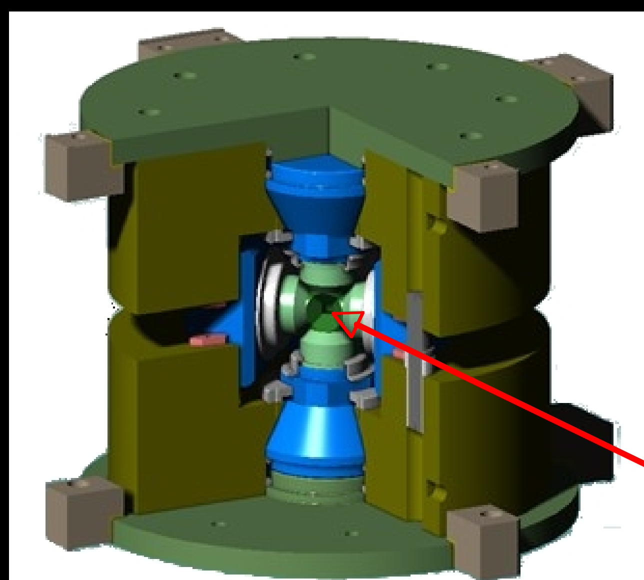
What about dislocation creep?

Dislocation creep is generally controlled by climb - and this is also a diffusion controlled mechanism.



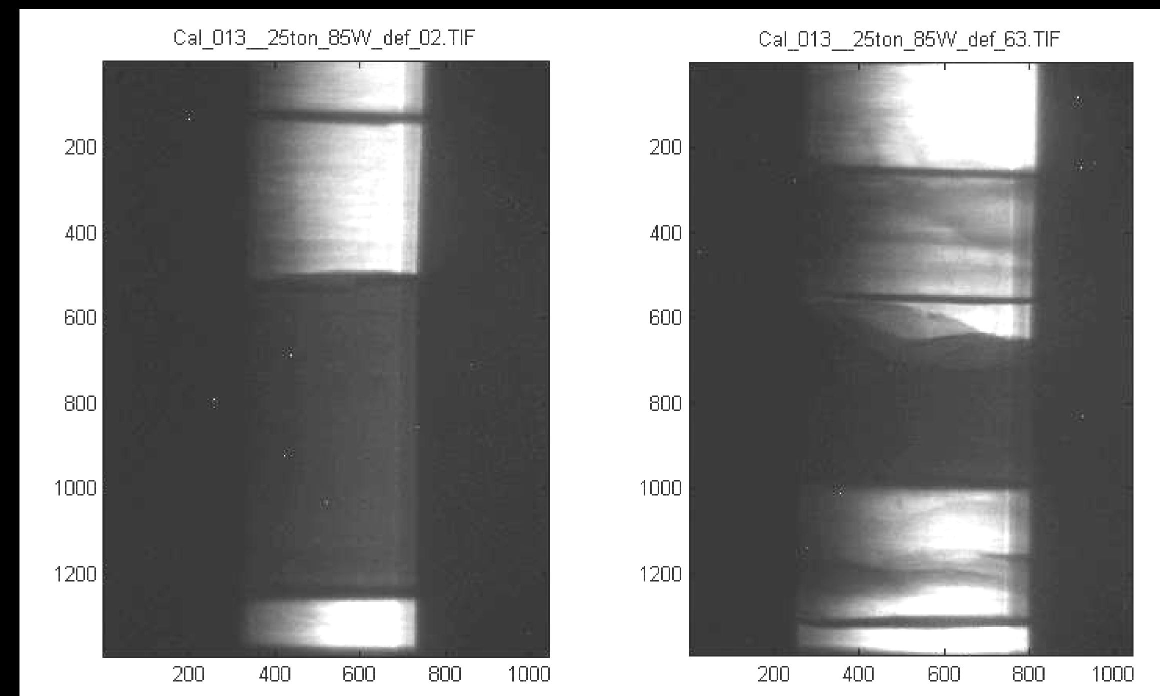
So the much faster diffusion of Si in the [100] direction in post-perovskite relative to post-perovskite should make it creep faster too - i.e., post-perovskite should be up to 4 orders of magnitude weaker than perovskite.

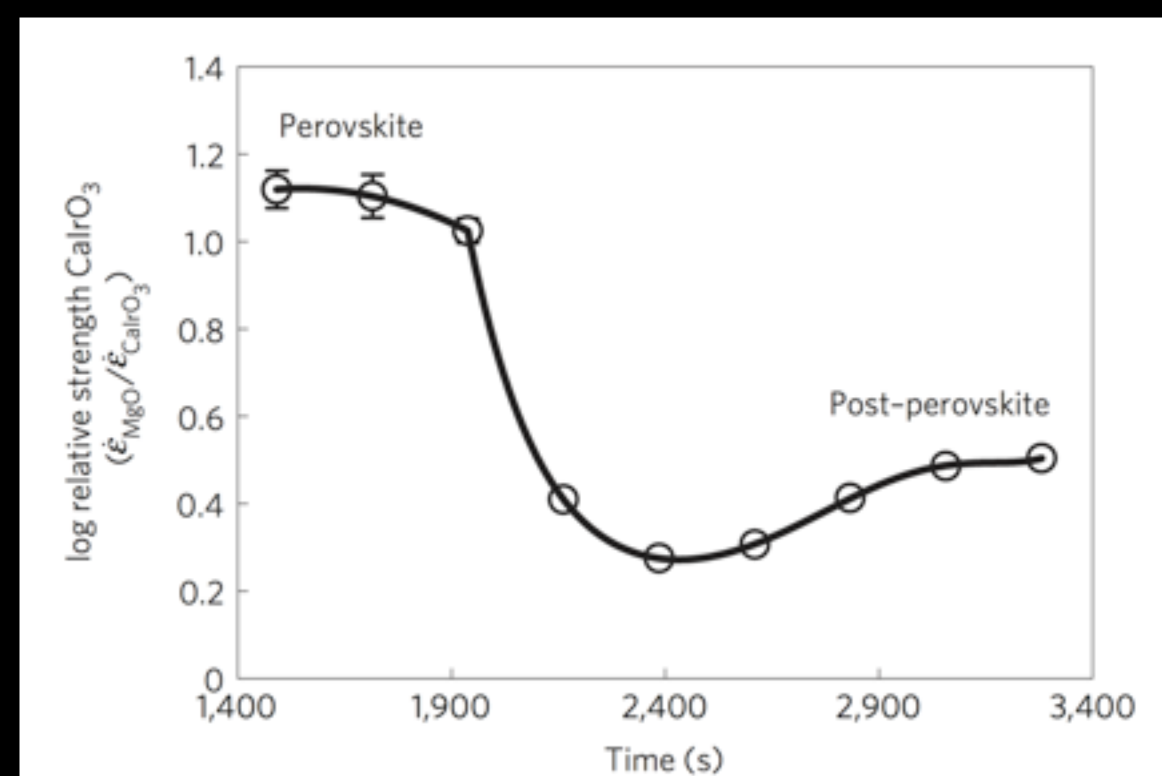
Experimental creep rates in transforming $CaIrO_3$



COMPRES beamline at the NSLS

Hunt et al, Nature Geoscience 2009





Other implications for weak post-perovskite:

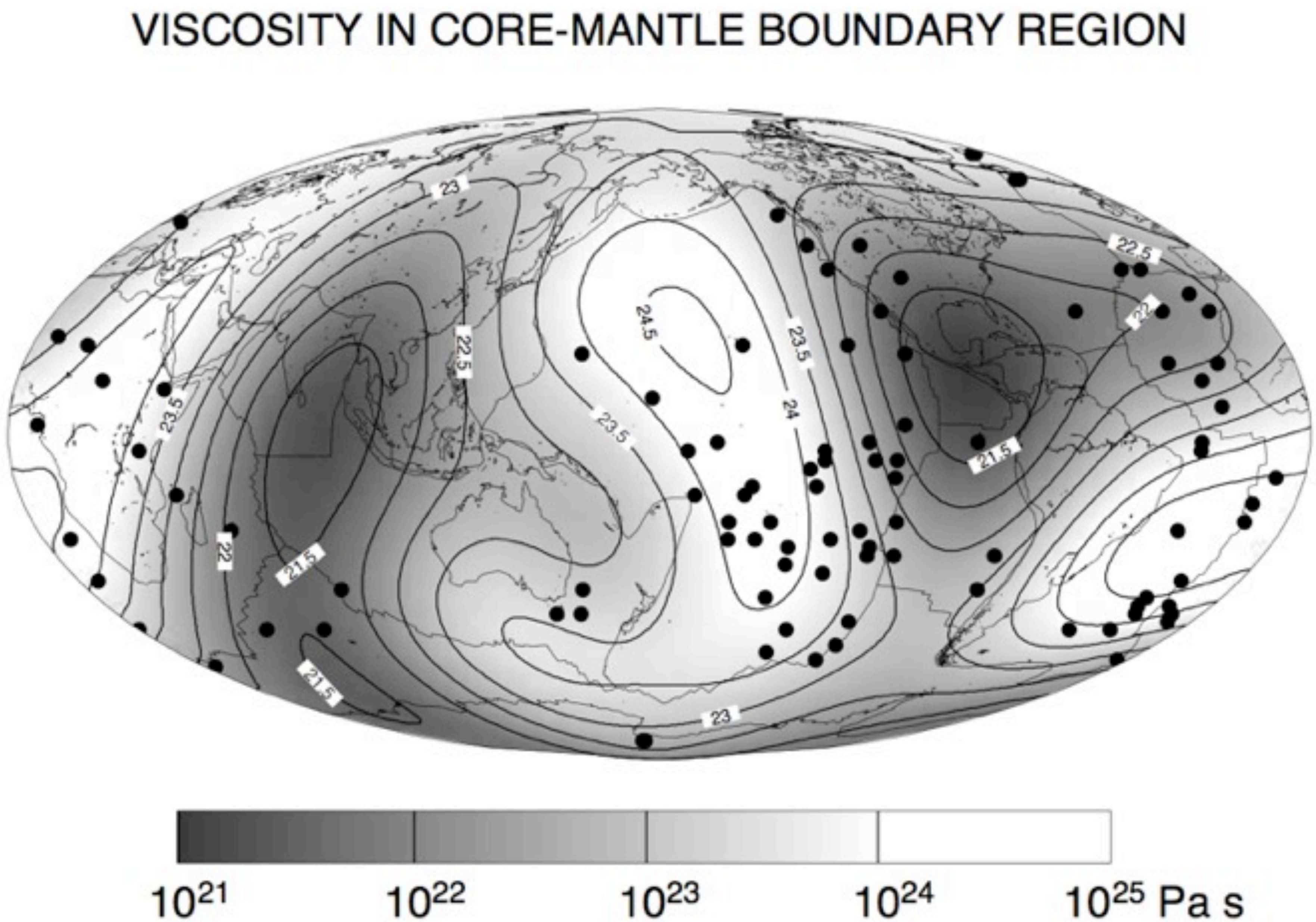
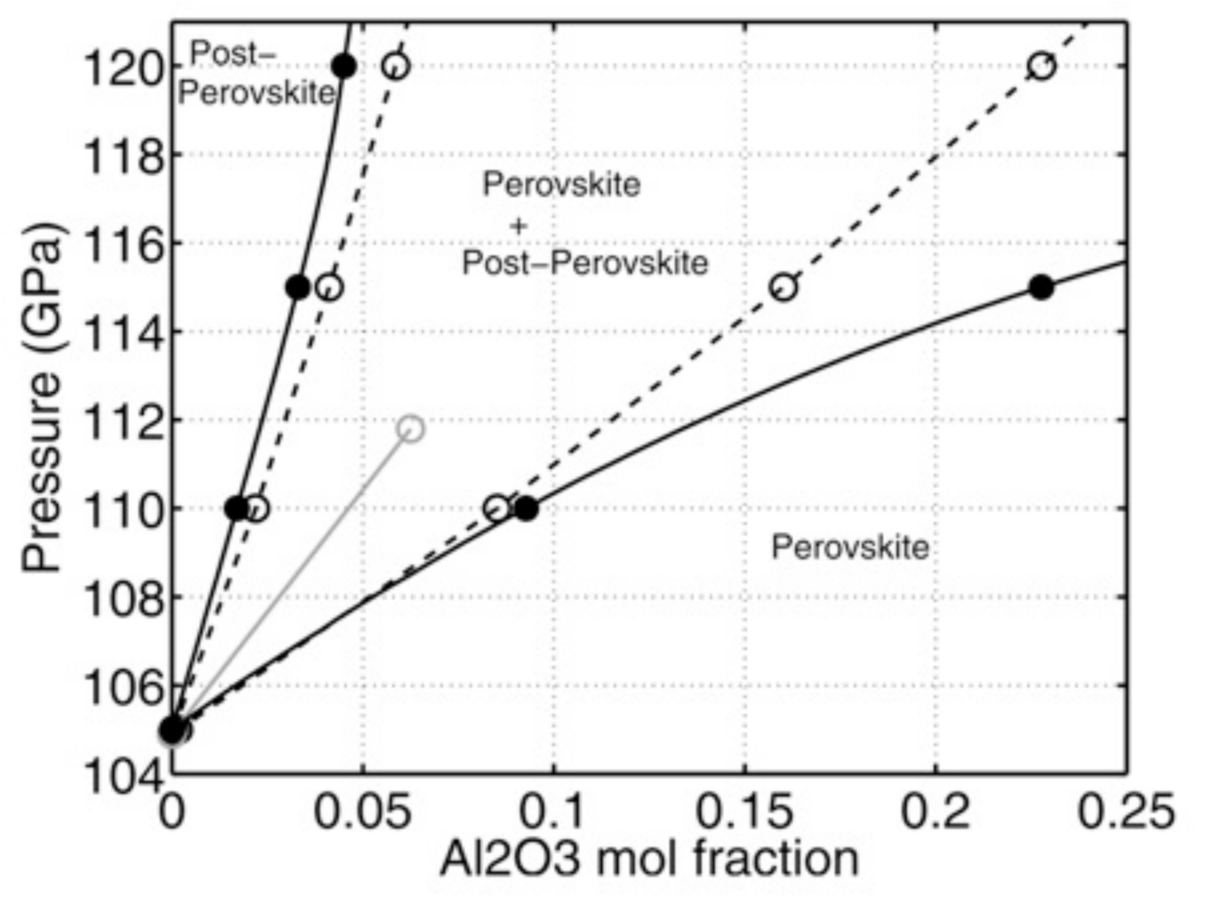


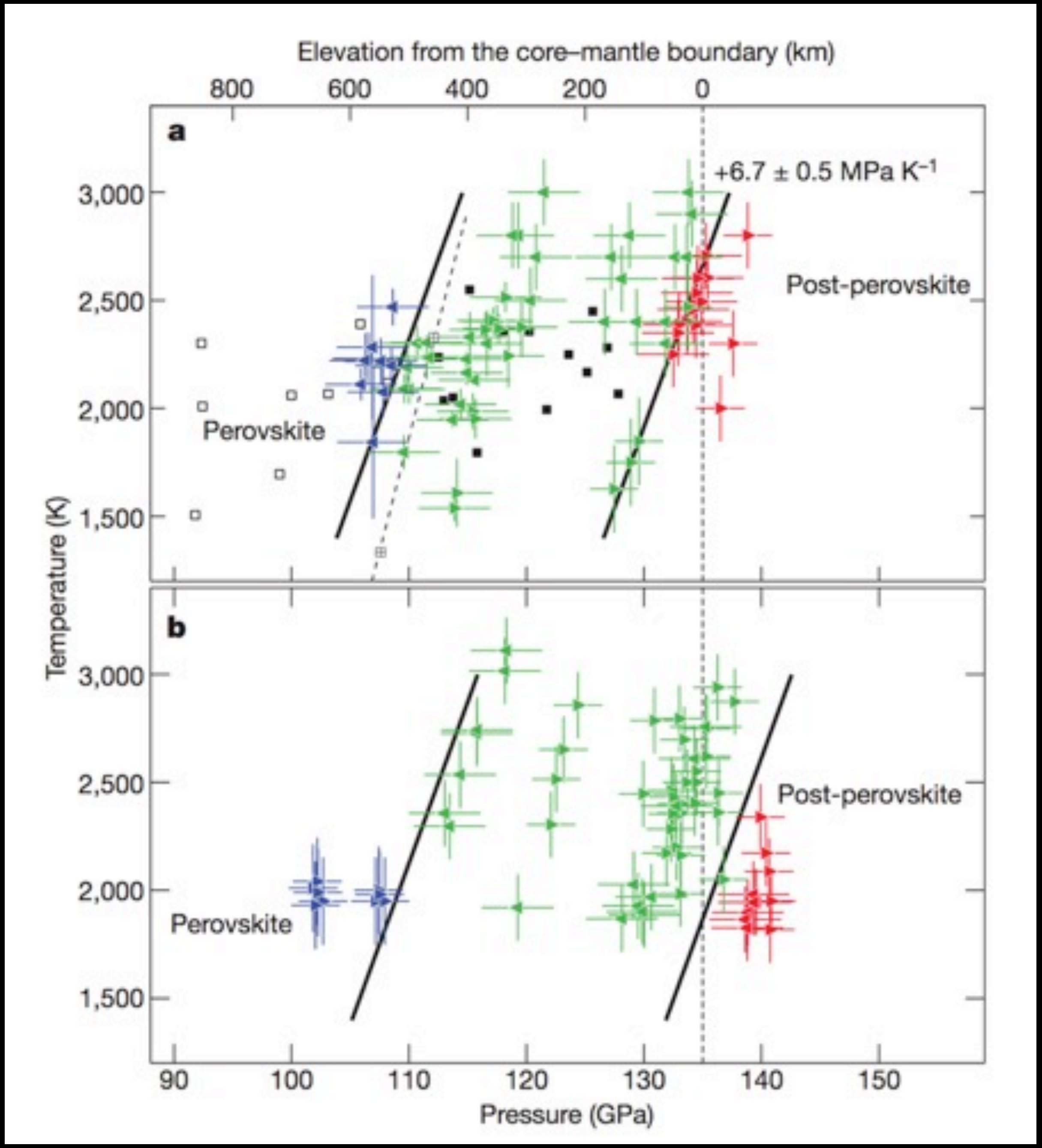
Fig. 2. Lateral viscosity variations in the core-mantle boundary region obtained from the inversion of the geoid. The viscosity (in Pa s) is plotted in logarithmic scale. The dots mark the positions of known hotspots (after *Nataf and Ricard, 1996*).

Cadek and Fleitout (2005)

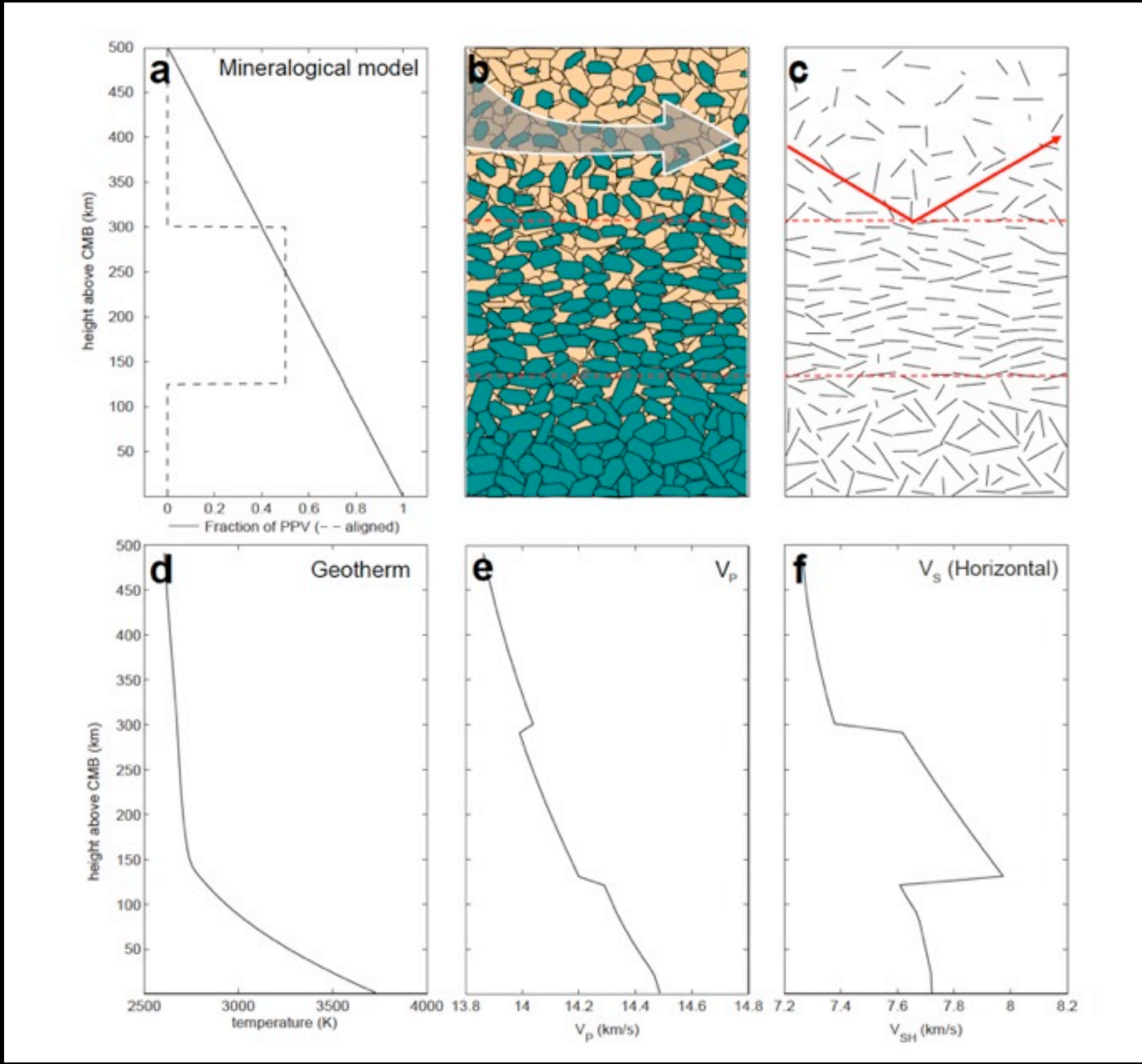
Is the phase transition too wide to be consistent with a sharp seismic refector?



Akber-Knutson et al, (2005)

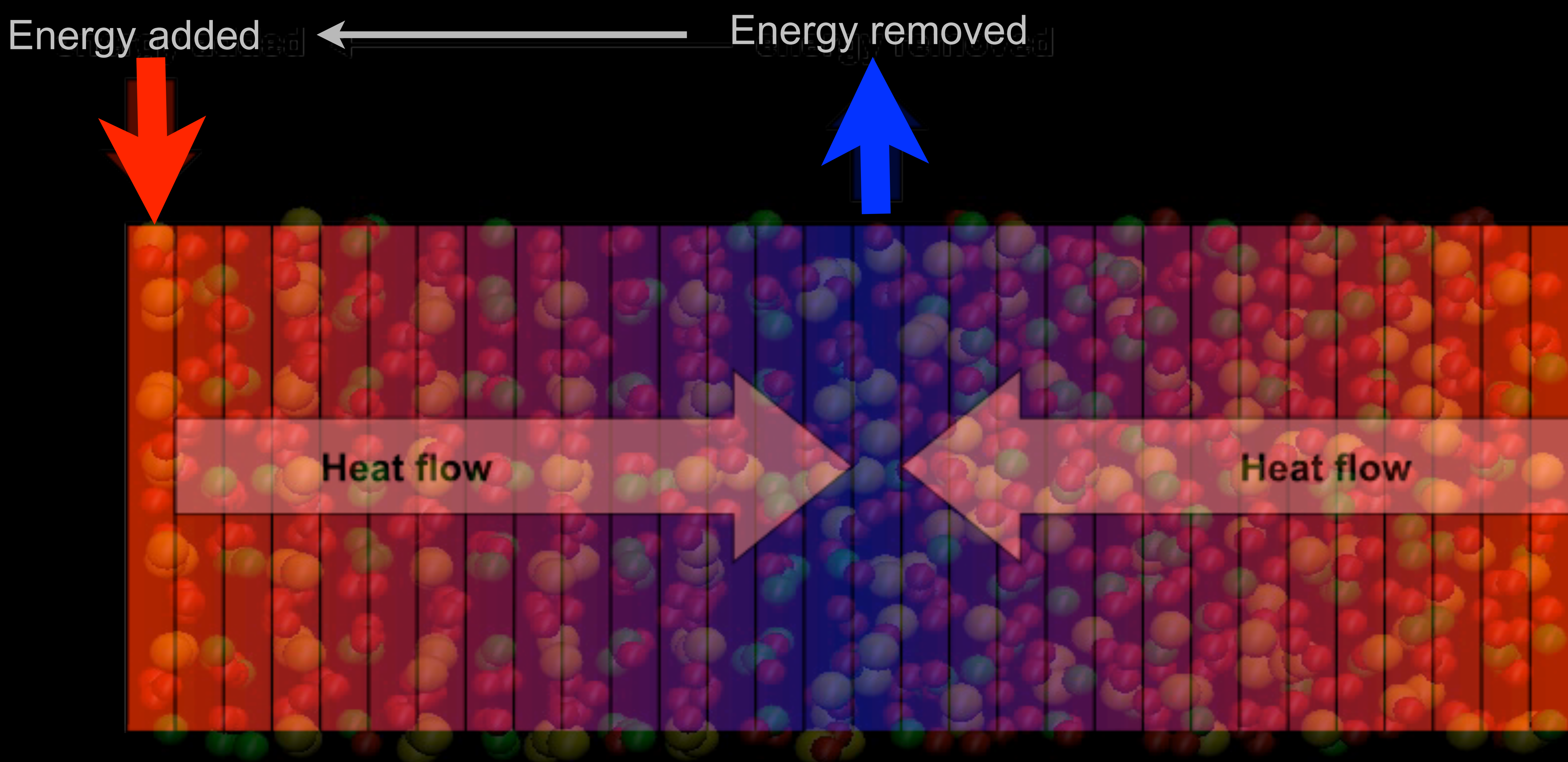


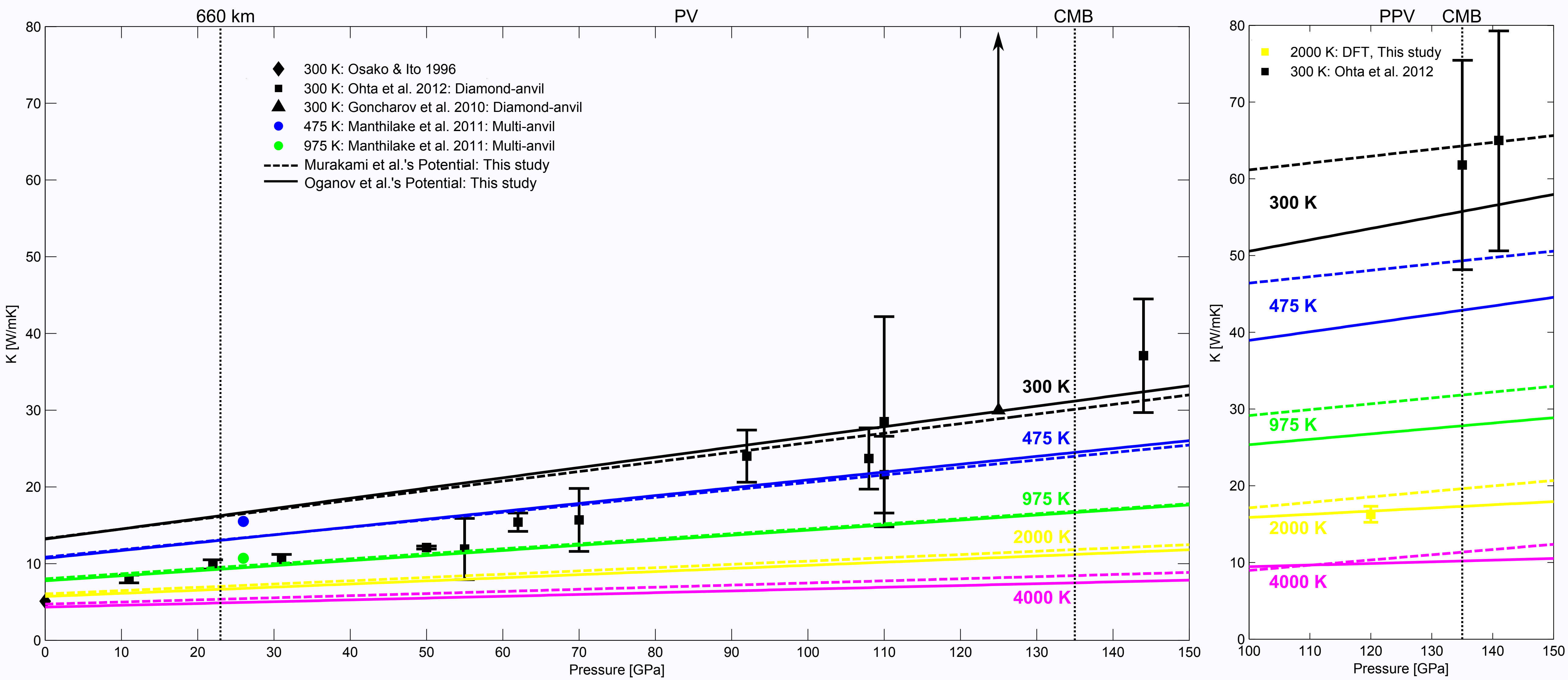
Catalli et al (2009)

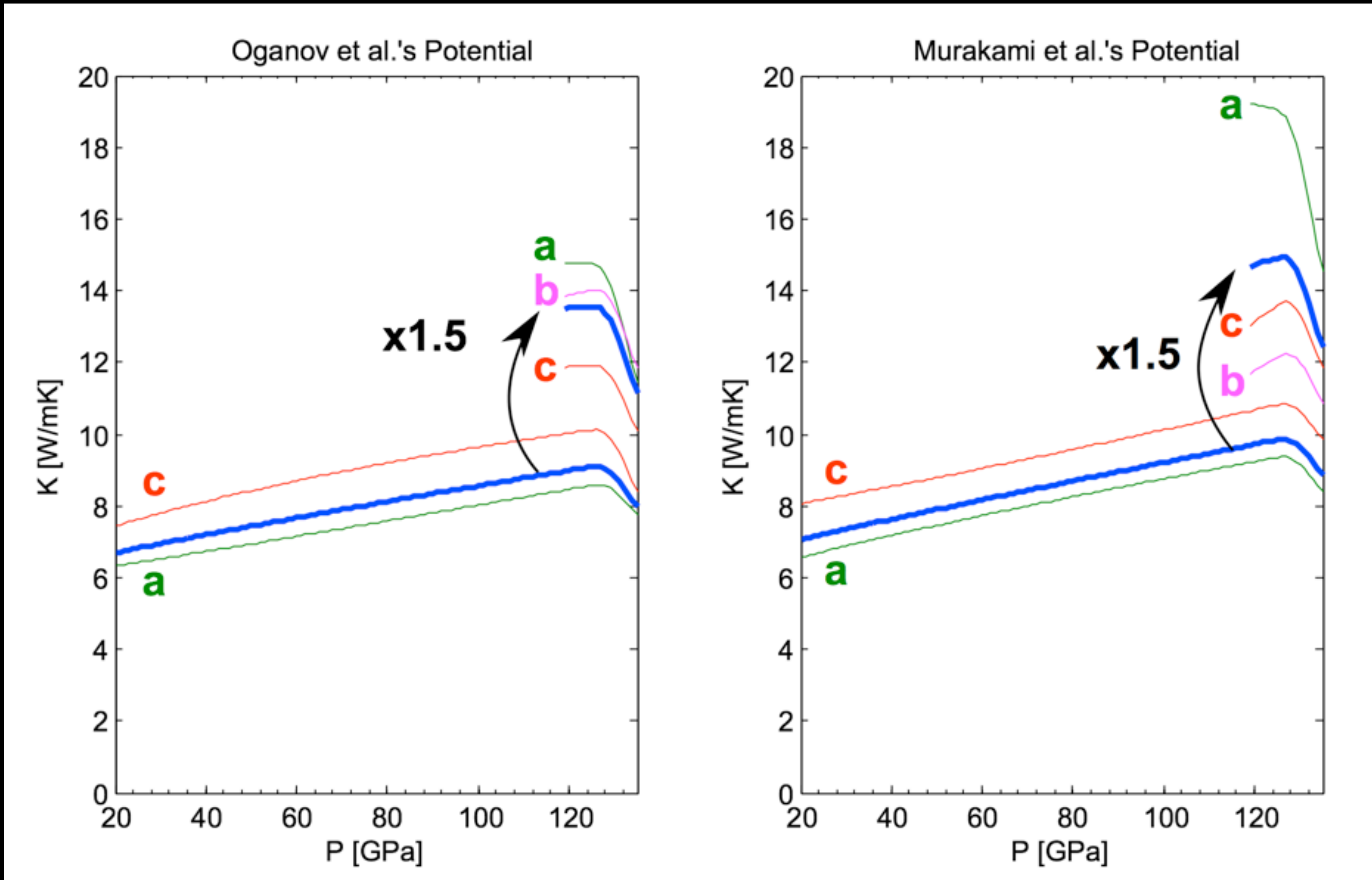


Ammann, Brodholt, Wookey and Dobson, Nature (2010)

Thermal conductivity (k)




660 km
PV
CMB
PPV
300 K: Osako & Ito 1996
300 K: Ohta et al. 2012: Diamond-anvil
300 K: Goncharov et al. 2010: Diamond-anvil
475 K: Manthilake et al. 2011: Multi-anvil
975 K: Manthilake et al. 2011: Multi-anvil
Murakami et al.'s Potential: This study
Oganov et al.'s Potential: This study
2000 K: DFT, This study
300 K: Ohta et al. 2012
300 K
475 K
975 K
2000 K
4000 K
K [W/mK]
Pressure [GPa]


Oganov et al.'s Potential
Murakami et al.'s Potential
K [W/mK]
P [GPa]
x1.5
a
b
c
a
c
a
c
b
c
a
x1.5

Flow model

↘

Anisotropy (LPO)

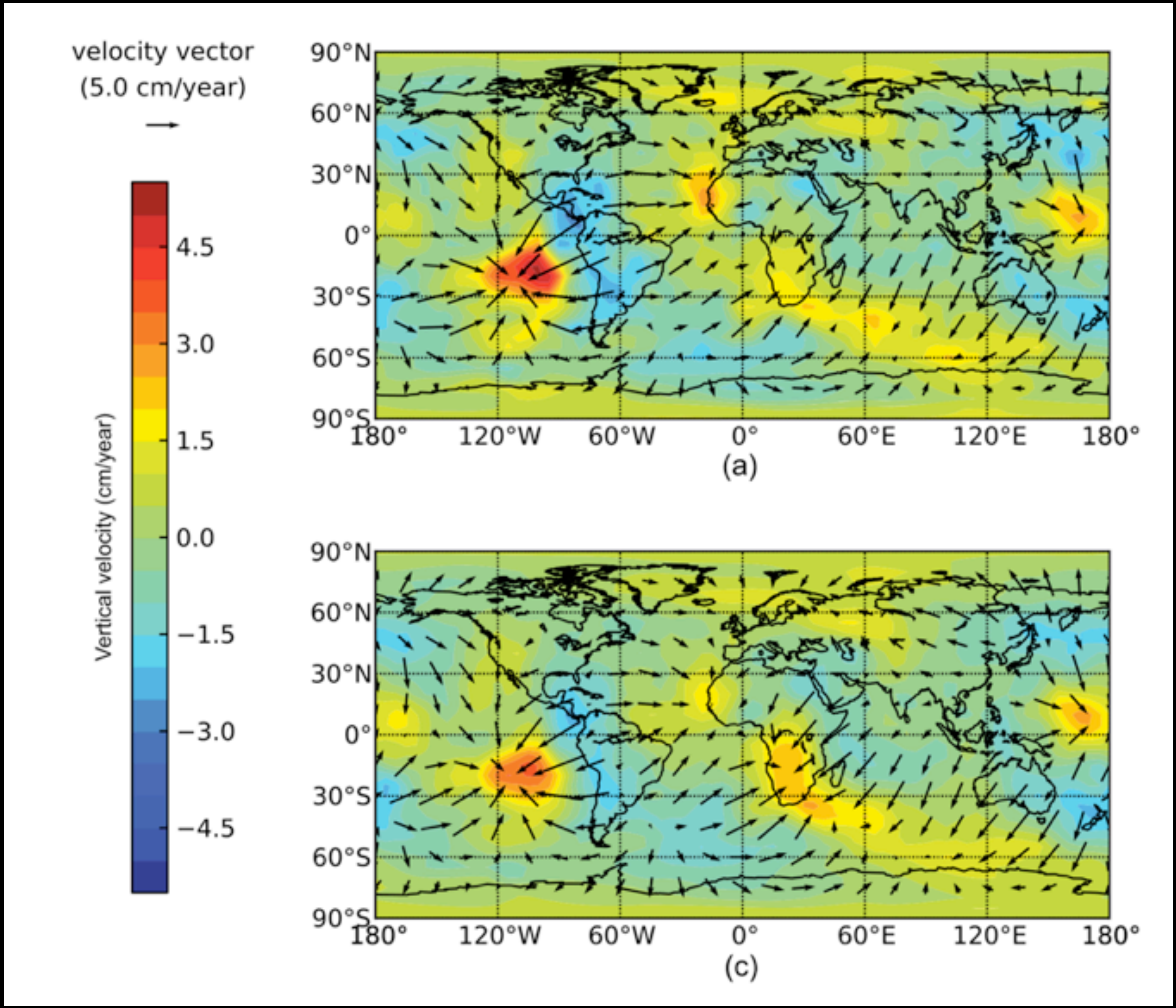
↘

Conductive heat flow

↘

Implications?

Flow Model



from Walker et al, 2011
and
Simmons et al
(2007,2008)

Anisotropy
Walker et al (2011)

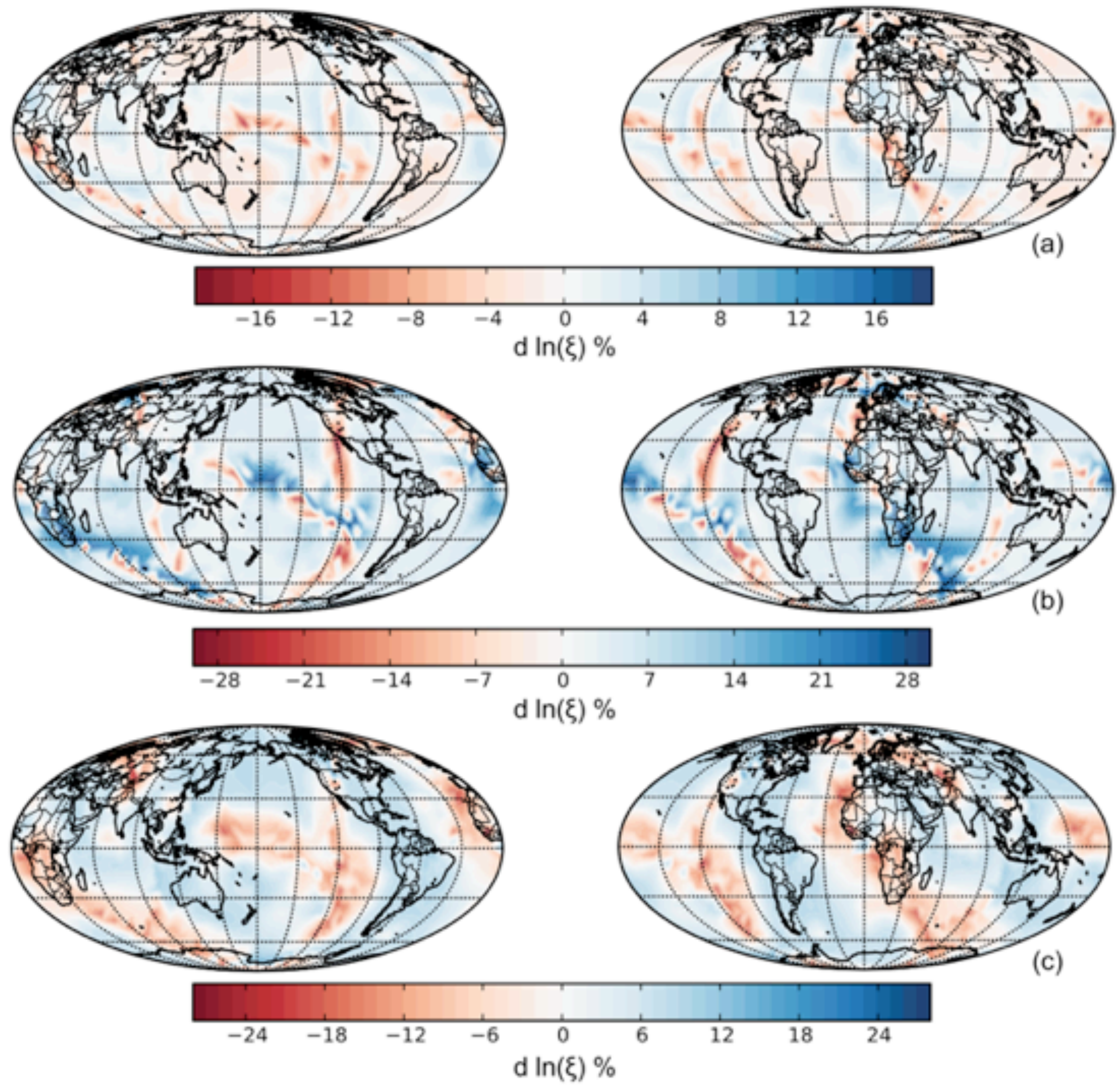
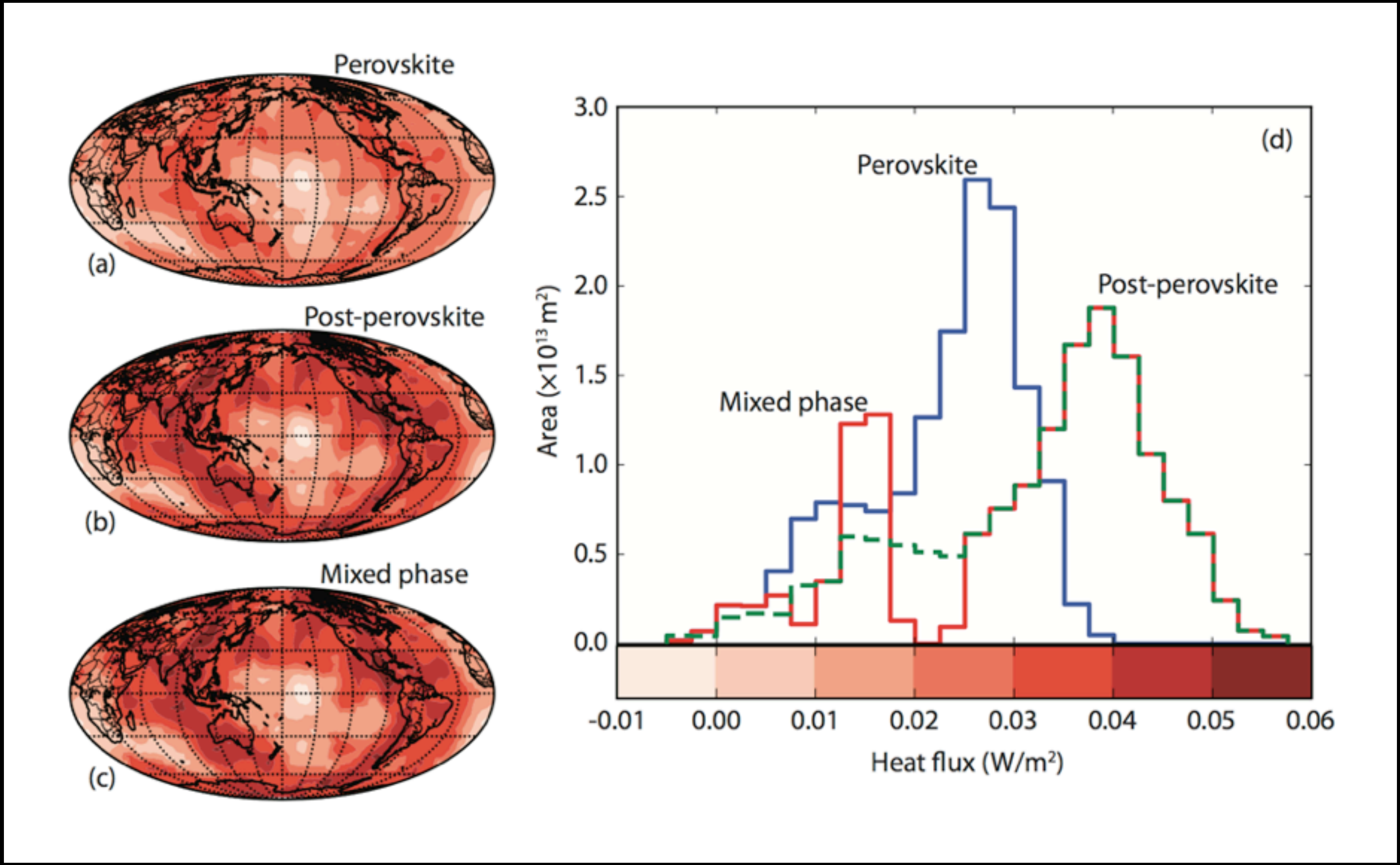
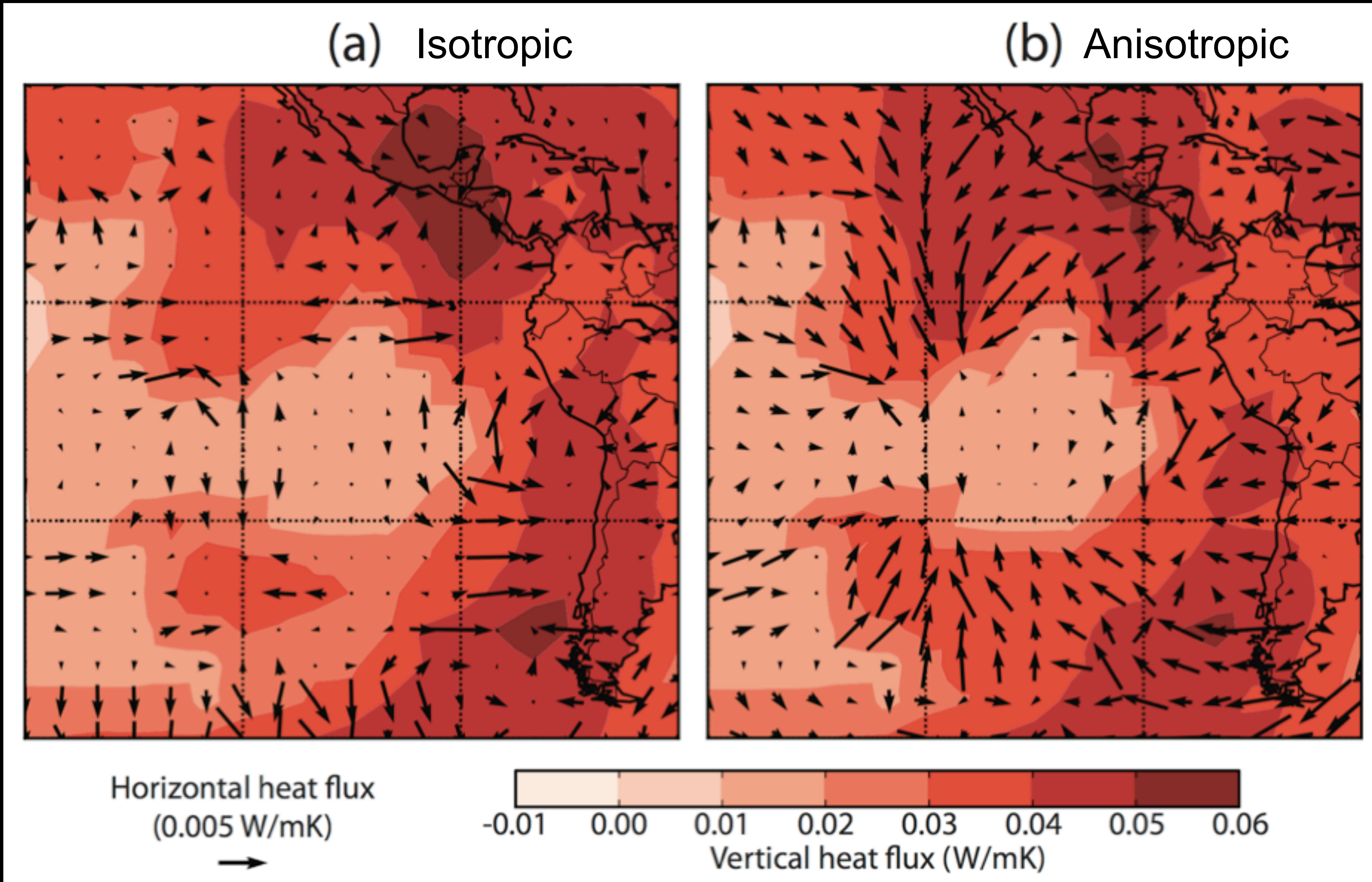


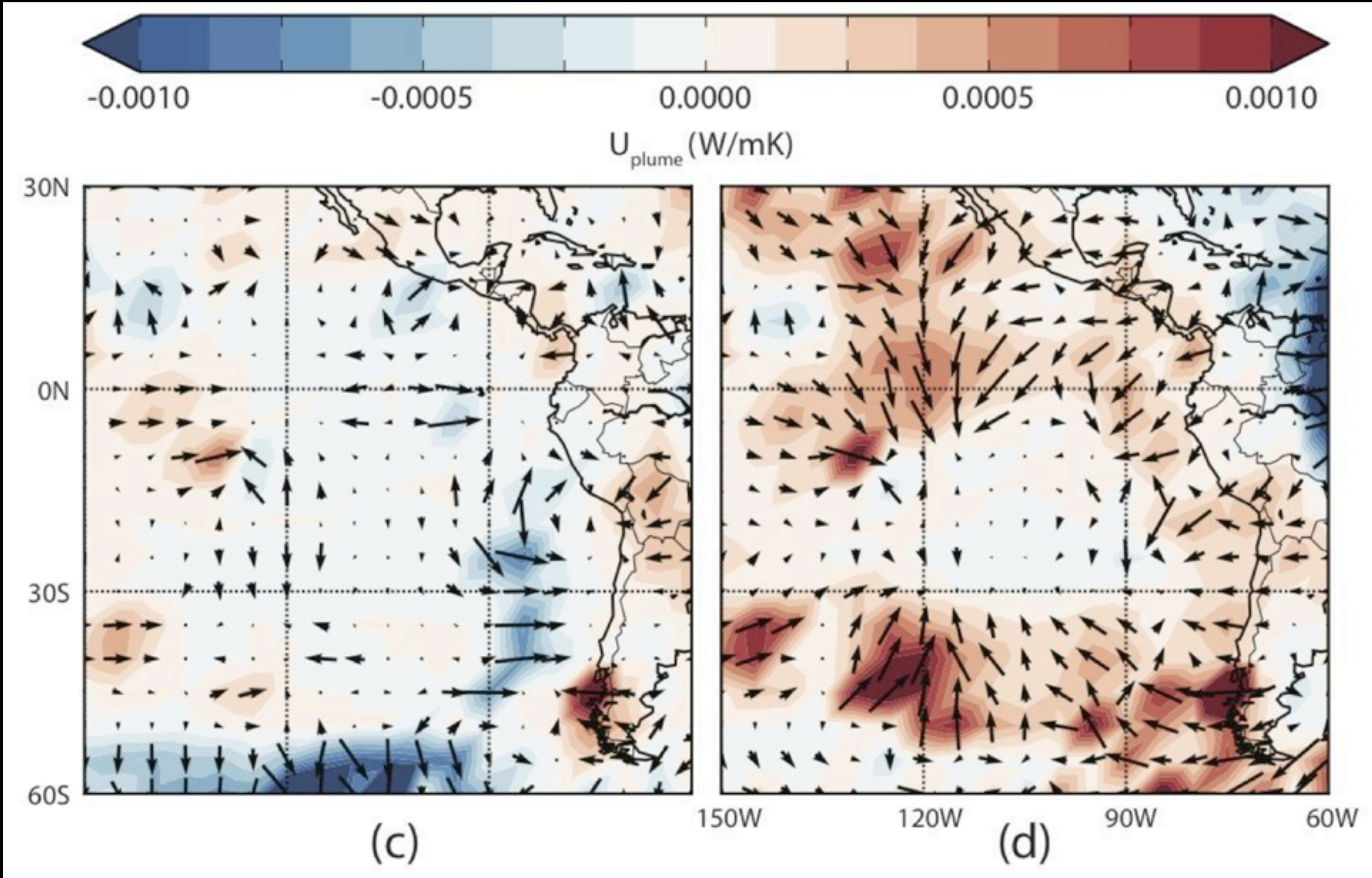
Figure 5. Calculated anisotropy, expressed as ln(ξ), for flow model TX2008.V1 75 km above the CMB with a temperature independent perovskite to post-perovskite phase transition 150 km above the CMB and three different single crystal plasticity models favoring dislocation motion on (010), (001) and (100). (a) TX2008.V1.P010; (b) TX2008.V1.P001; (c) TX2008.V1.P100.



Total heat flow = 3.5, 4.9, 4.8 TW for three models



Does this matter?


-0.0010
-0.0005
0.0000
0.0005
0.0010
U plume (W/mK)
30N
0N
30S
60S
150W
120W
90W
60W
(c)
(d)

Conclusions

- Can use ab initio methods to calculate diffusion rates of minerals difficult to measure experimentally
- Ferro-periclase is much weaker than perovskite throughout the mantle. Spin transition slightly weakens it further.
- Lower mantle viscosity could be controlled by ferro-periclase in areas of high strains.
- Post-perovskite has very anisotropic diffusion rates and is probably much weaker than perovksite
- Post-perovskite has somewhat anisotropic conductivity, which may help stabilise plumes.