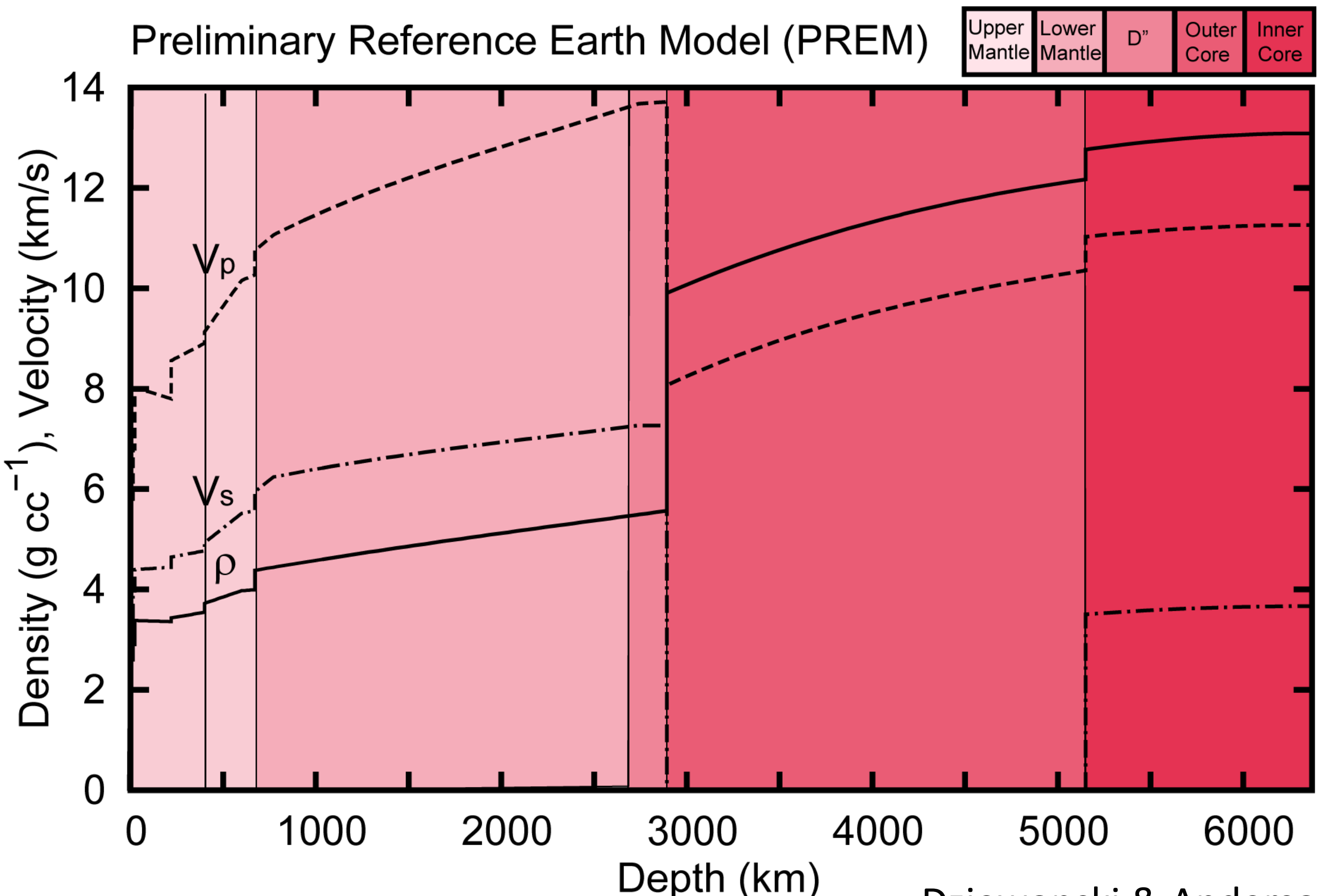
Spin crossovers in iron in lower mantle phases

Renata Wentzcovitch

Applied Physics and Applied Mathematics

Lamont Doherty Earth Observatory, Columbia University

1D-Seismic Model

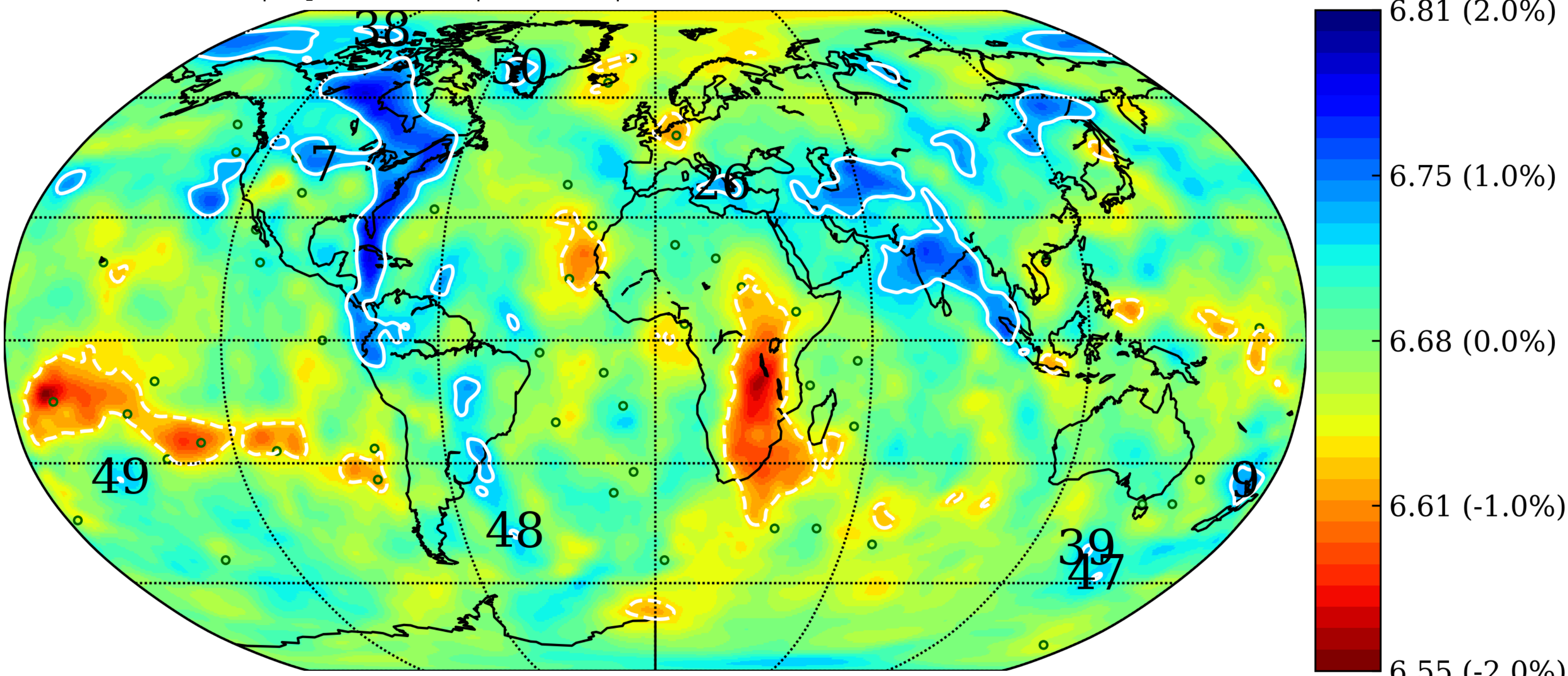


Dziewonski & Anderson, 1981

Making sense of mantle heterogeneities (Seismic Tomography)

S-model

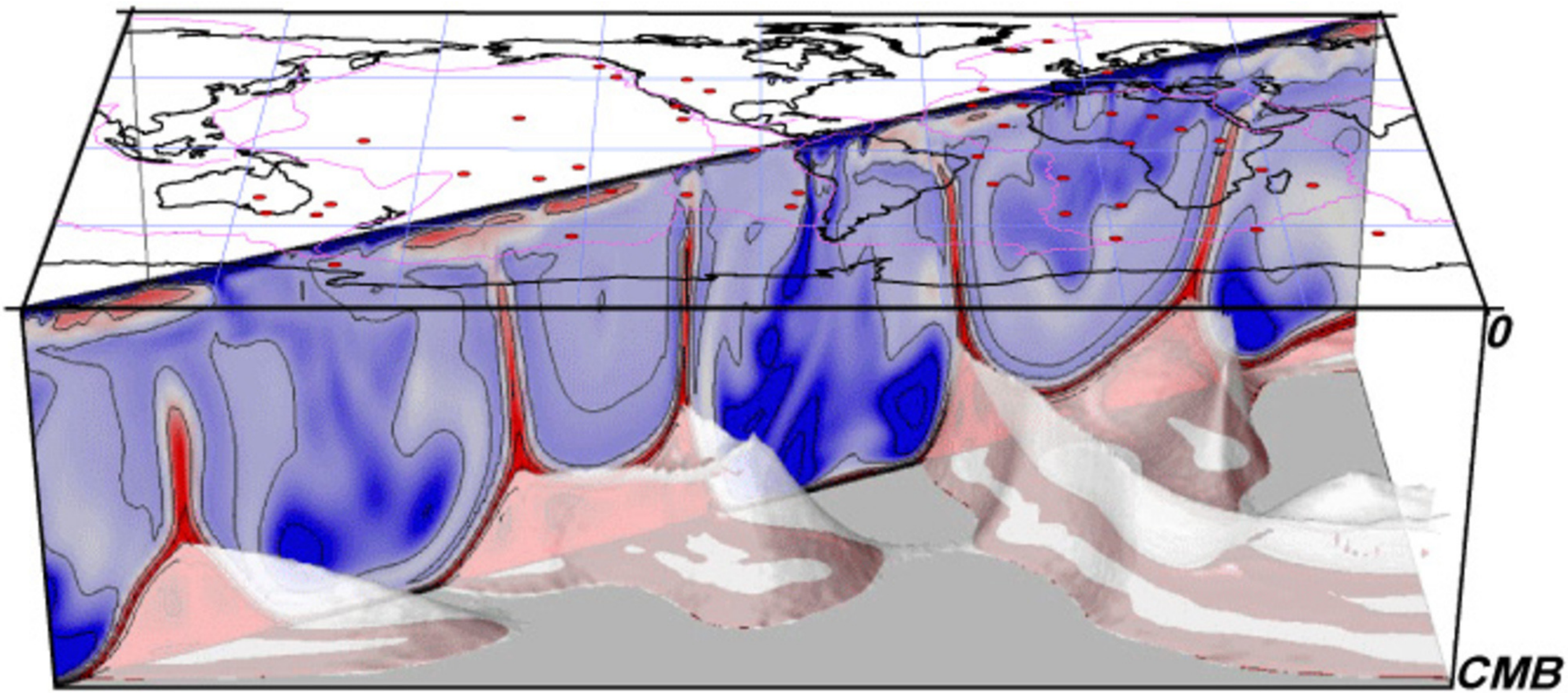
Parameter: vs | depth: 1500 km | ref: mean | threshold: <6.63 (dashed red), >6.73 (solid blue)



GLAD-M25 δV_S

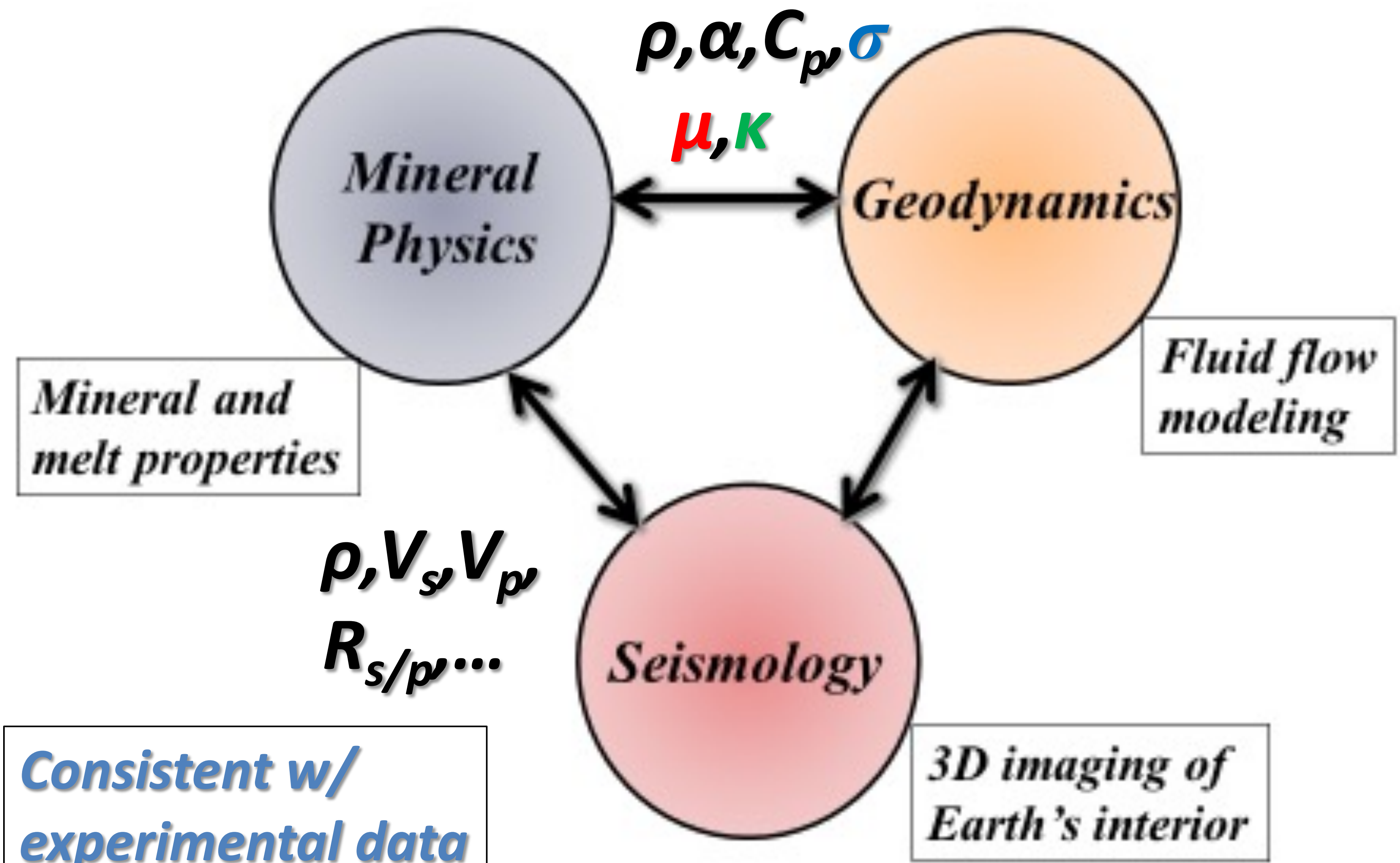
(Lei, Tromp, et al., 2021)

Thermochemical convection (need ρ, K, α, C_P, μ, κ)



(McNamara et al., 2014)

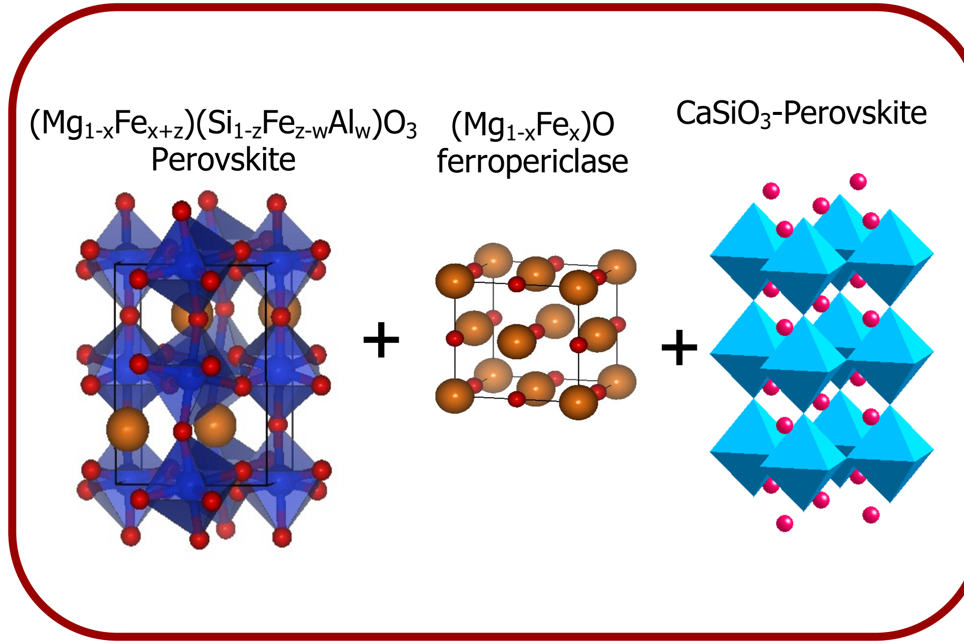
The Big Picture

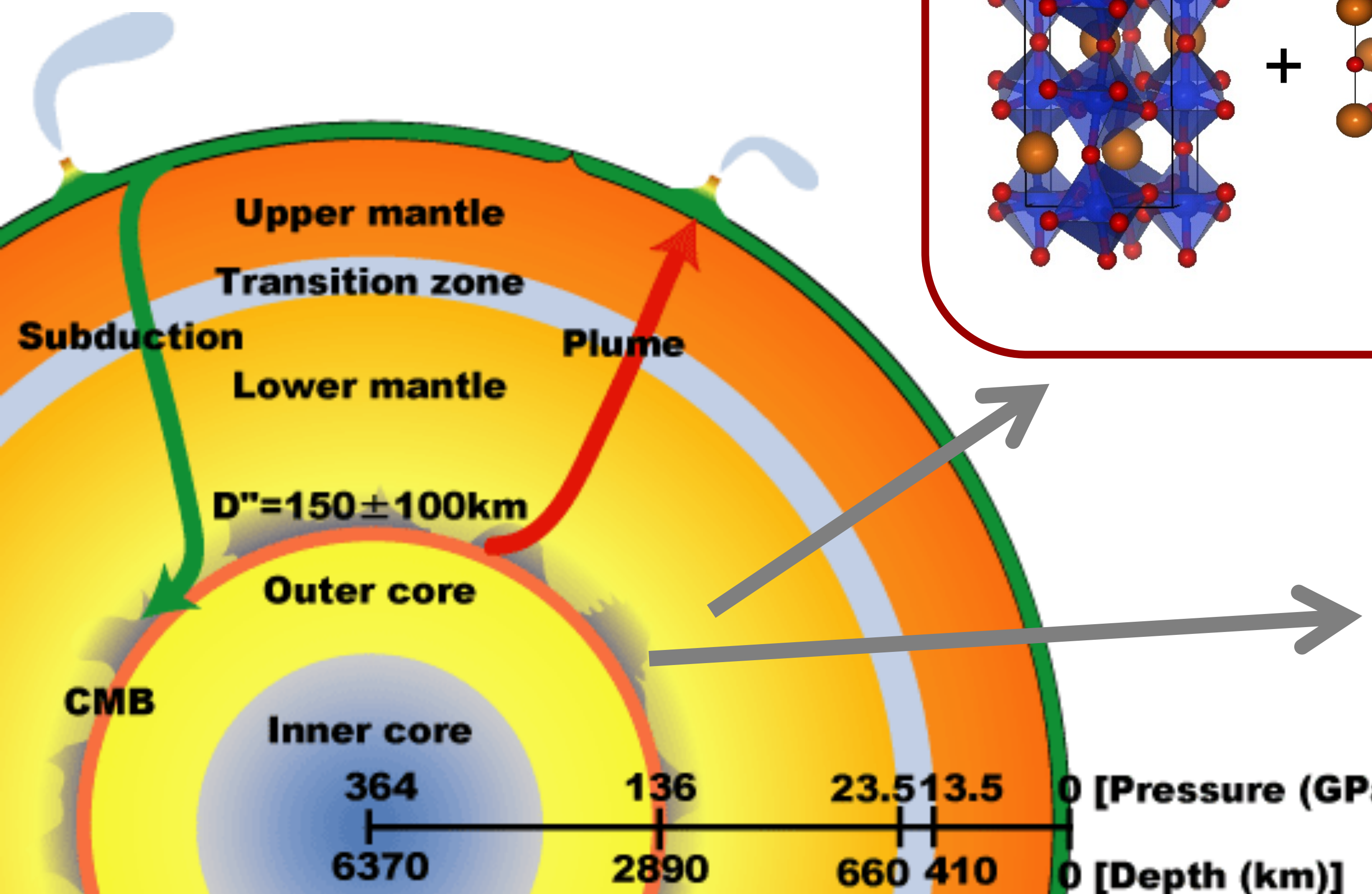


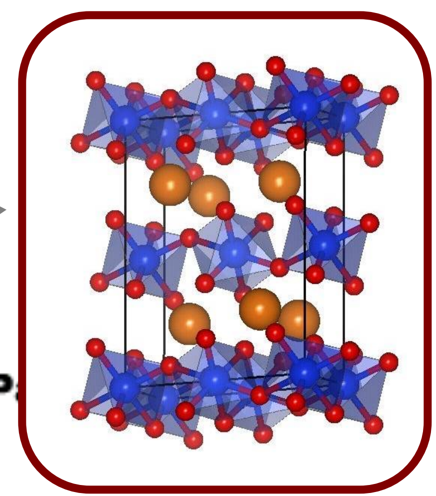
Consistent w/ experimental data

Earth's lower mantle

- Lower Mantle: Ferrosilicate perovskite + ferropericlase + $CaSiO_3$
- Low iron concentration (x~0.1)
- 2000 K < T < 4000 K
- 23 GPa < P < 135 GPa







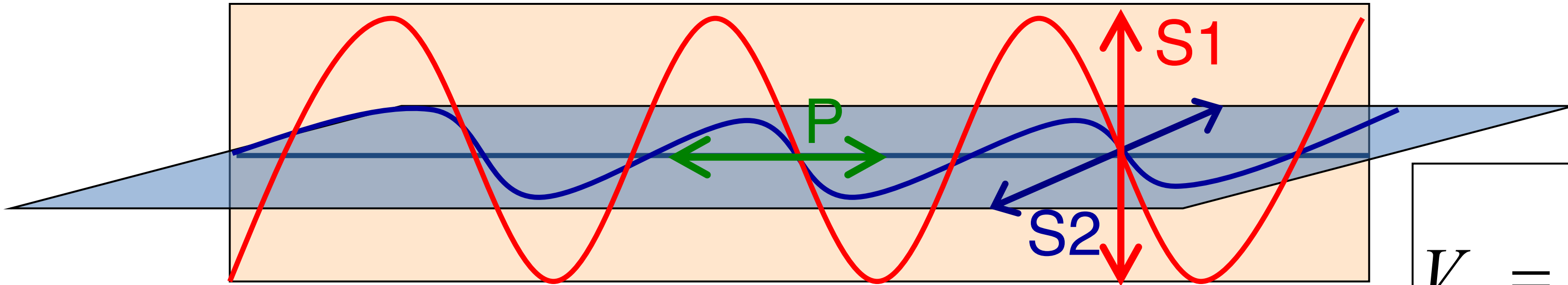
Body wave (acoustic) velocities

- Longitudinal waves (P-waves)
  (compressive waves)

$$V_P = \sqrt{\frac{K + \frac{4}{3}G}{\rho}}$$

- Transverse waves (S-waves)
  (shear waves)

$$V_S = \sqrt{\frac{G}{\rho}}$$



$$V_\varphi = \sqrt{\frac{K}{\rho}}$$

K and ***G*** from Voigt-Reuss-Hill bounds

Pressure induced spin “transition” in (Mg,Fe)O and $(Mg,Fe)SiO_3$

Iron Partitioning in Earth’s Mantle: Toward a Deep Lower Mantle Discontinuity

James Badro,[1] Guillaume Fiquet,[1] François Guyot,[1] Jean-Pascal Rueff,[2] Viktor V. Struzhkin,[3] György Vankó,[4] Giulio Monaco[4]

Science

AAAS

2003

Electronic Transitions in Perovskite: Possible Nonconvecting Layers in the Lower Mantle

James Badro,[1*] Jean-Pascal Rueff,[2] György Vankó,[3] Giulio Monaco,[3] Guillaume Fiquet,[1] François Guyot[1]

Science

AAAS

2004

Outline

- Spin crossovers
- Thermodynamics model of a spin crossover: (Mg,Fe)O
- (Mg,Fe)SiO_3 (it is not what it seems…)
- Spin crossover in (Mg,Fe)(Si,Fe)O_3 and (Mg,Fe)(Si,Al)O_3
- Manifestation of a crossover in the mantle
- Acknowledgments

Methods

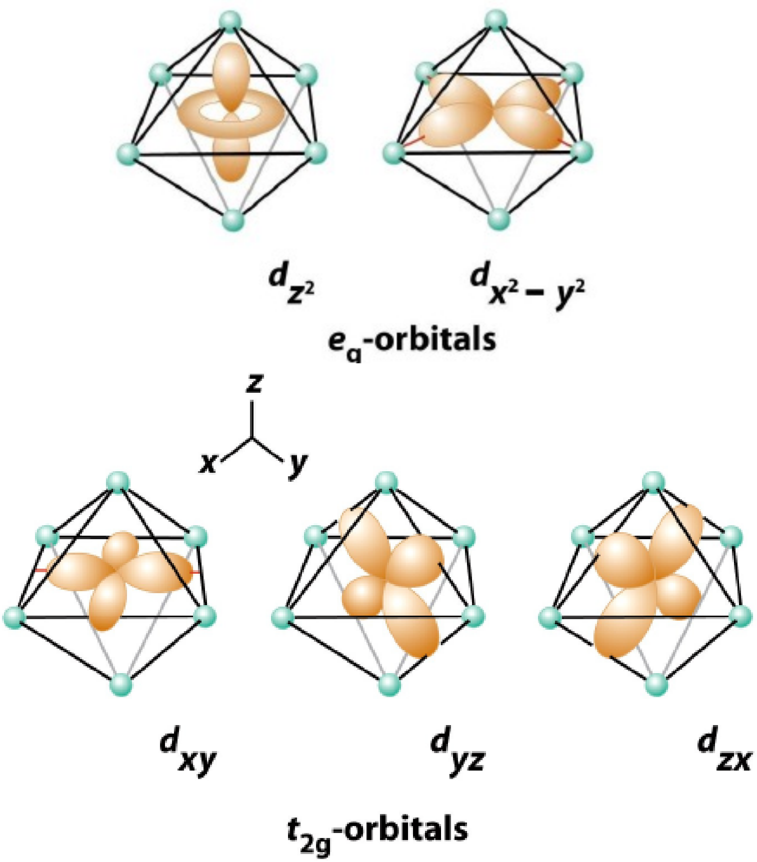
- *Ab initio variable cell shape molecular dynamics*
  *(Wentzcovitch and Martins, 1993)**
- *Self-consistent DFT+U*
  (Cococcioni and de Gironcoli, 2005)
- *Density Functional Perturbation Theory + U for phonons*
  (Floris, de Gironcoli, Gross, Cococcioni, 2011)
- *Quantum ESPRESSO and Wien2K (all electron code)*
  (Giannozzi, ..., Wentzcovitch, 2009, 2016; Blaha et al., 2010)*
- *QHA to compute vibrational free energy*
  *(Karki, Wentzcovitch, de Gironcoli, Baroni, 2000)**
- *Semi-analytical method to compute acoustic velocities*
  *(Wu & Wentzcovitch, 2011)**
- *Quasi-ideal solid solution*
  *(Wu, Justo, da Silva, Wentzcovitch, 2009)**

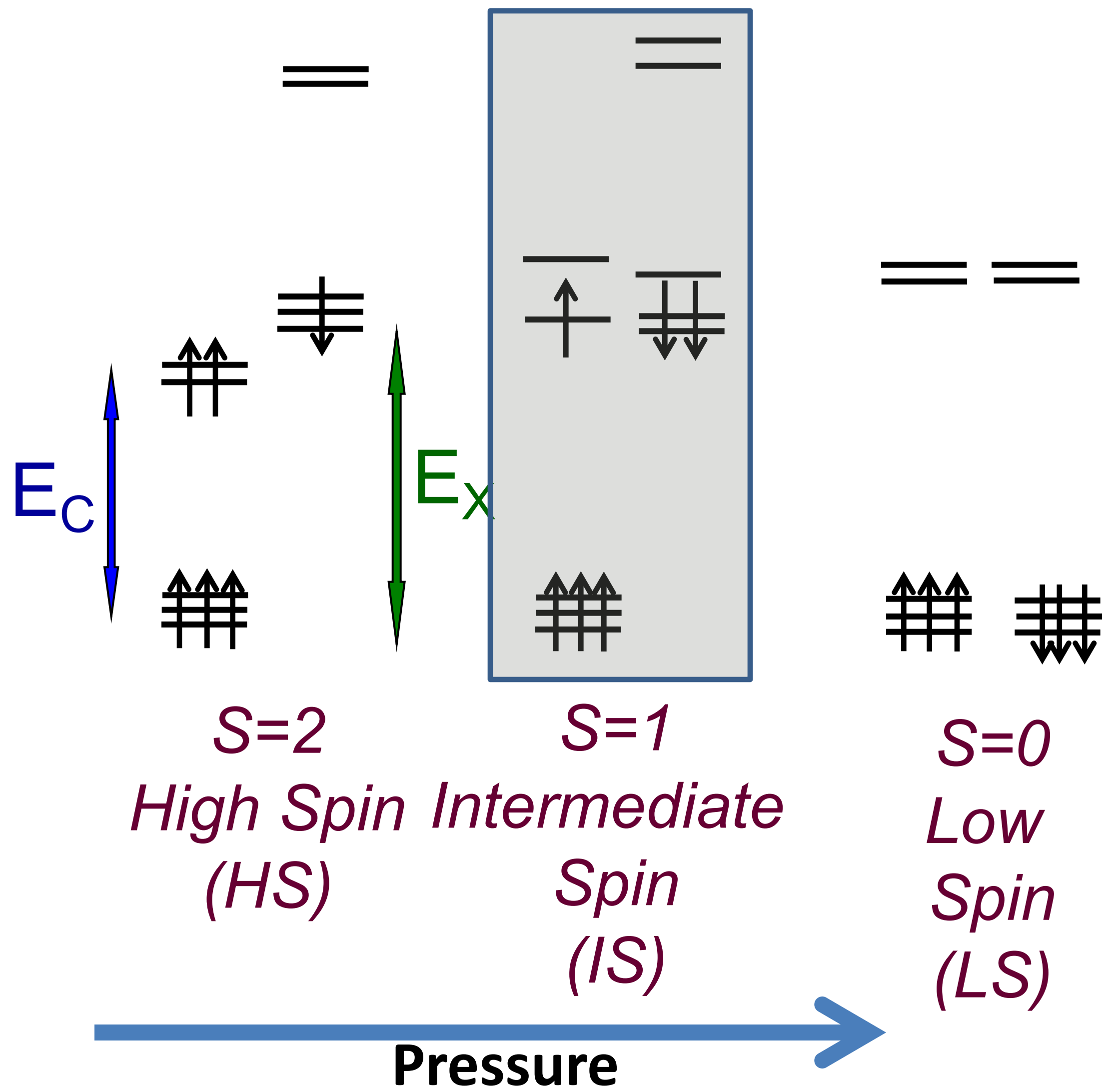
Spin transition (or crossover)

Fe^{2+} $3d^6$

d-electrons in crystal field

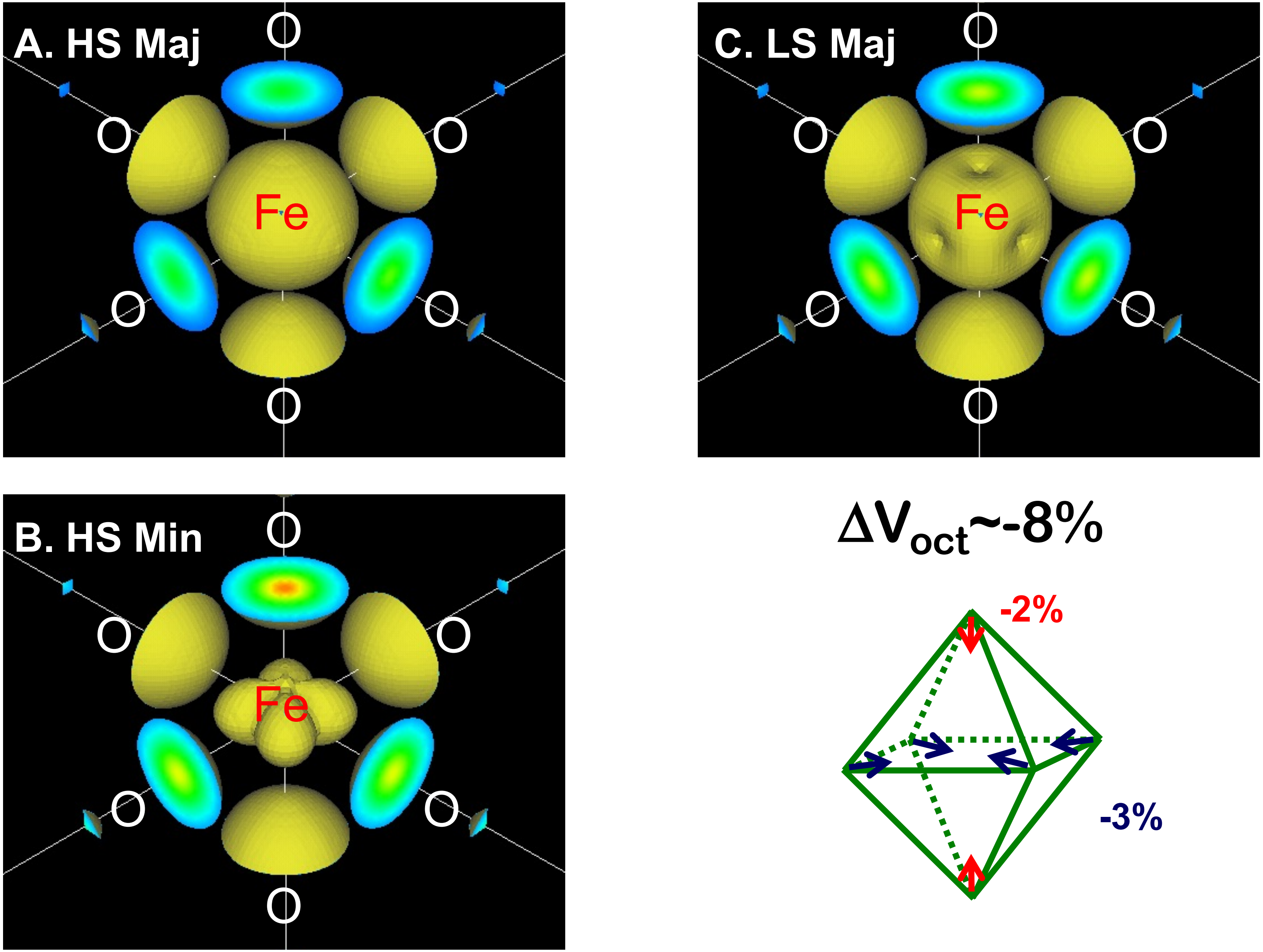
$M^{m+} \rightarrow$ [core] $3d^n$



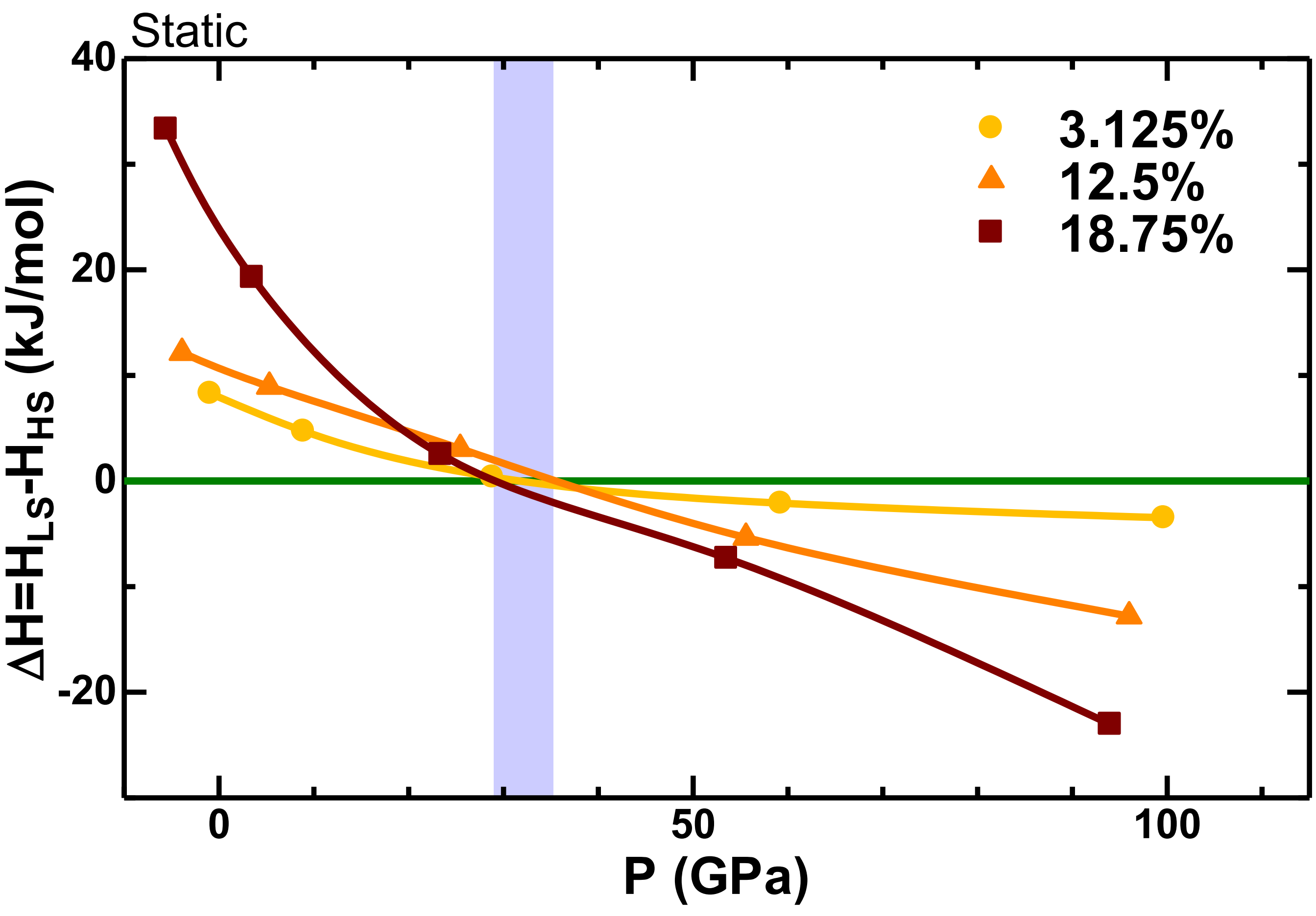


Ferropericlase

ρ_{el} around Fe^{2+} (Isosurface:ρ_{el}=0.3 e/Å^3)



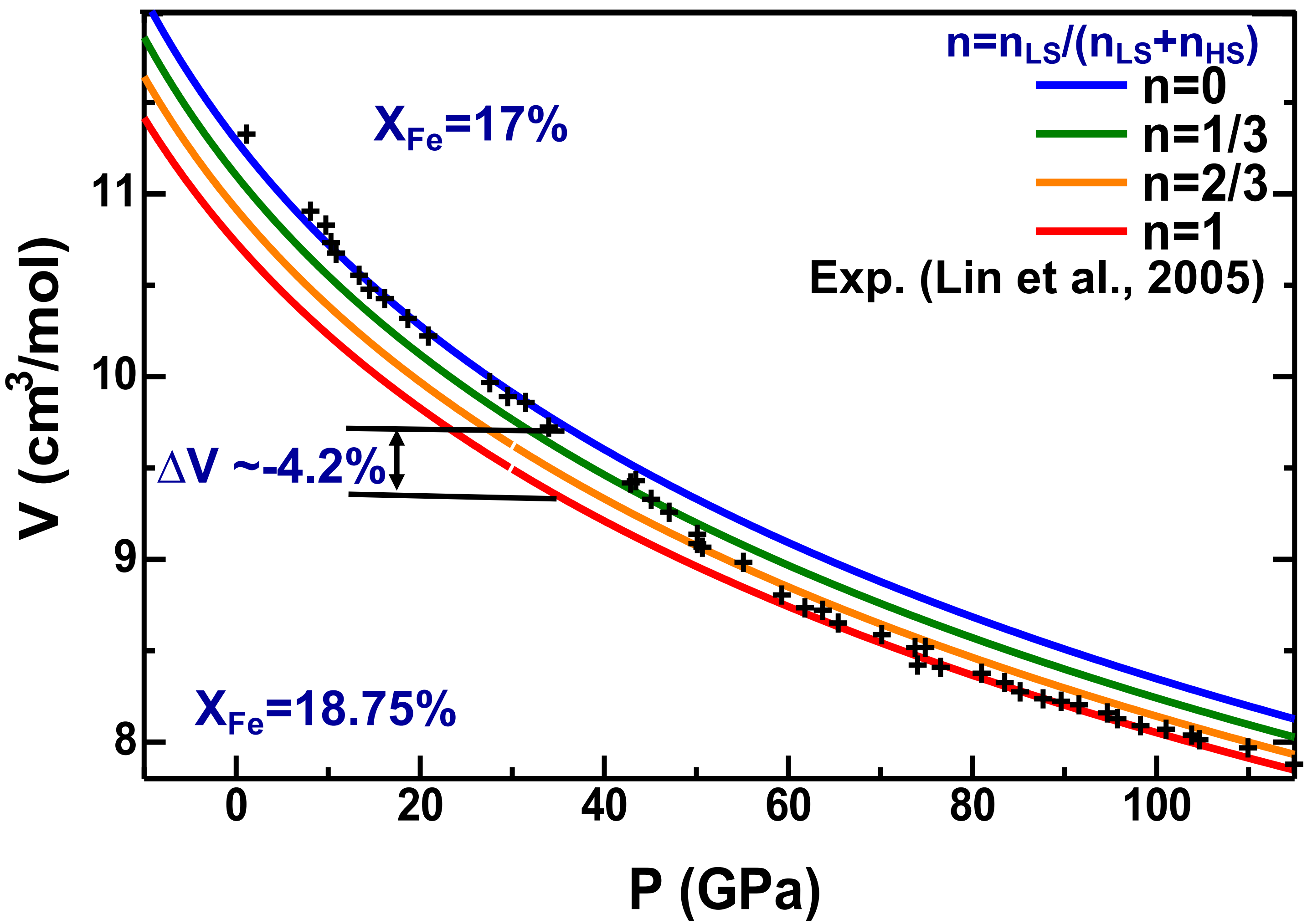
HS-to-LS "transition"



$$P_T = 32 \pm 3 \text{ GPa}$$

Tsuchiya, de Gironcoli, da Silva, and Wentzcovitch, PRL (2006)

Static equation of state



Tsuchiya et al., PRL (2006)

$$\Delta V_{HS\text{-}LS} = -2.22\ nX_{Fe}\ \mathrm{cm^3/mol}$$

Thermodynamics

Thermodynamics Method

- VDoS and F(T,V) within the QHA

$$F(V,T) = E(V) + \sum_{qj} \frac{\hbar\omega_{qj}(V)}{2} + k_B T \sum_{qj} \ln\left(1 - \exp\left[-\frac{\hbar\omega_{qj}(V)}{k_B T}\right]\right)$$

N-th (N=3,4,5…) order *isothermal* (eulerian or logarithm) finite strain EoS

$$P = -\left[\frac{\partial F}{\partial V}\right]_T$$

$$S = -\left[\frac{\partial F}{\partial T}\right]_V$$

$$G = F - TS + PV$$

Ideal solid solution of HS and LS ferropericlase (x_{Fe} = cte)

$$n = n_{LS}/(n_{HS}+n_{LS})$$

$$V = (1-n)V_{HS} + nV_{LS}$$

$$G = (1-n)G_{HS} + nG_{LS} + G_{mix}$$

$$G_{HS/LS} = F_{HS/LS} + PV_{HS/LS}$$

$$G_{HS/LS} = F_{HS/LS}^{(stat+vib)} + F_{HS/LS}^{mag} + PV_{HS/LS}$$

$$F_{HS/LS}^{el} = -TS_{HS/LS}^{mag}$$

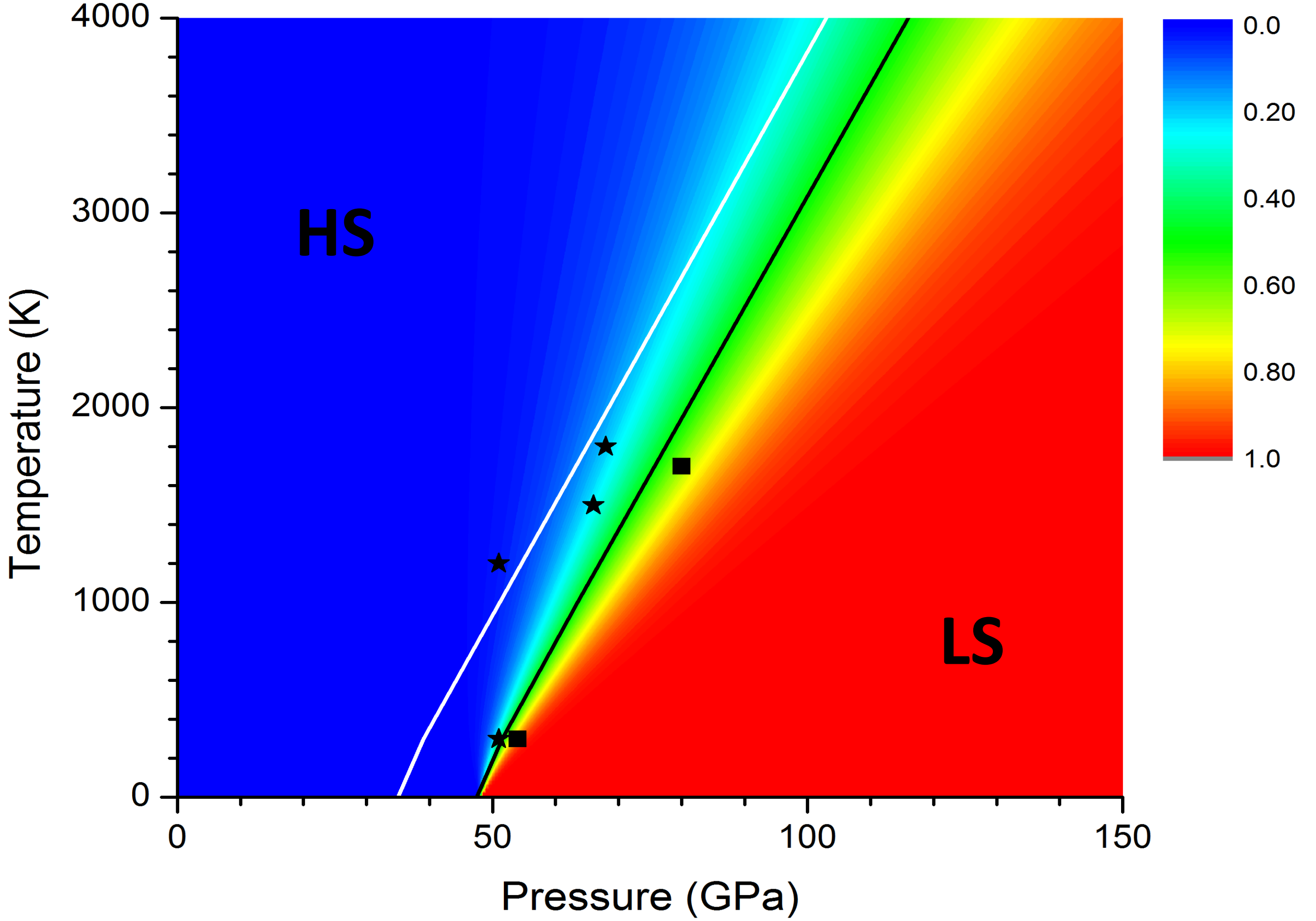
$$G_{mix} = -TS_{ideal}$$

Free energy minimization

$$n(P,T) = \frac{1}{1 + m(2S+1)\exp\left[\dfrac{\Delta G_{HS-LS}^{st+vib}}{X_{Fe} k_B T}\right]}$$

LS fraction n(P,T)

(Tsuchiya et al., 2006, Wentzcovitch *et al.*, *PNAS*, 2009)



■ ***Komabayashi et al., EPSL (2010)* x=0.10**

★ ***Lin et al., Science* (2007) x=0.17**

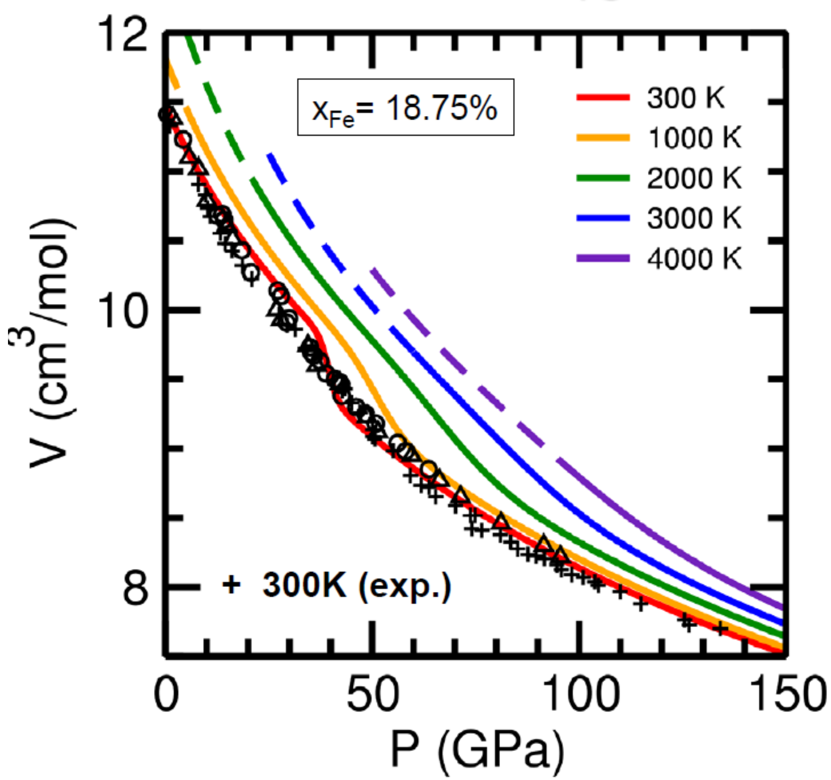
Spin crossover in ferropericlase (Fp)

- One really needs to investigate the EOS of Fp at high T.
- The pressure range of K_s anomalies increases with T
- It also shifts crossover pressure range to higher P

Wentzcovitch, Justo, Wu, da Silva Yuen, Kohlstedt, *PNAS* 2009

Exp: Crowhurst et al, Science 2006

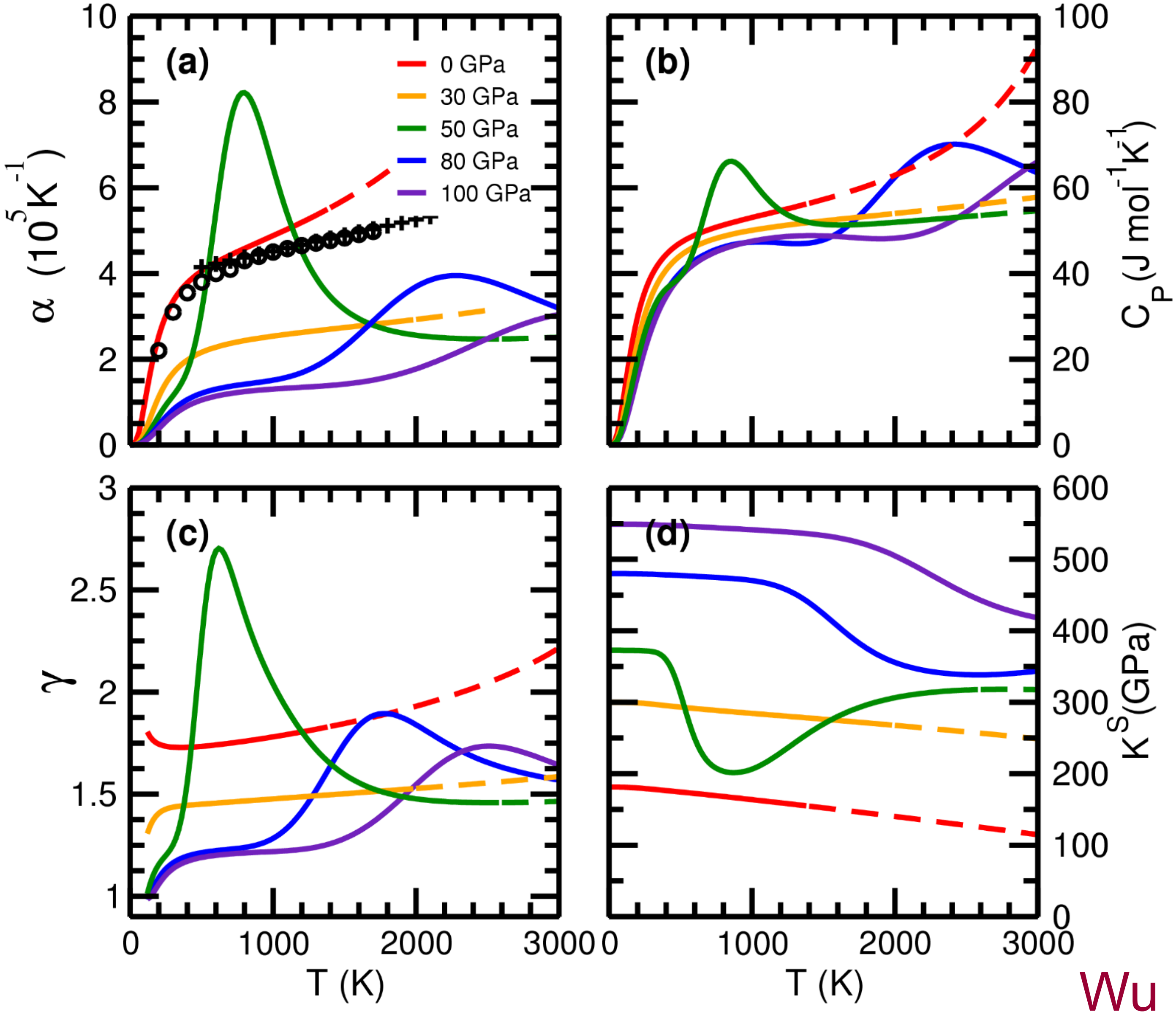
Volume V(P,T) for x_{Fe}= 18.75%



+ 300K (exp.)

+ Experiments (Lin *et al.*, *Nature*, 2005) (x_{Fe}=17%, RT)
o and Δ (Fei *et al.*, GRL, 2007) (X_{Fe}=20%, RT)

Thermodynamics properties x_{Fe}= 18.75%



Experiments
(o x_{Fe}=0 and += 40%)

300K (exp.)

Wu et al, PRB 2009

Elastic anomalies in $Mg_{1-x}Fe_xO$

- *Impulsive stimulated scattering: softening of C_{11}, C_{12}, and C_{44} (Crowhurst et al., 2008, Science AAAS)*

- *Brillouin scattering: softening of C_{11} and C_{12}, but not C_{44} (Marquardt et al., 2009, Science AAAS)*

- *Inelastic X-ray scattering: softening of C_{44} and C_{12}, but not C_{11} (Antonangelli et al., 2011, Science AAAS)*

High temperature elasticity

(Wentzcovitch et al., PNAS 2009; Wu, Justo, and Wentzcovitch, PRL 2013)

$$V(P,T,n) = nV_{LS}(P,T) + (1-n)V_{HS}(P,T)$$

High temperature elasticity

(Wentzcovitch et al., PNAS 2009; Wu, Justo, and Wentzcovitch, PRL 2013)

$$V(P,T,n) = nV_{LS}(P,T) + (1-n)V_{HS}(P,T)$$

- **Compressibility:**

$$\frac{V(n)}{K(n)} = n\frac{V_{LS}}{K_{LS}} + (1-n)\frac{V_{HS}}{K_{HS}} - (V_{LS} - V_{HS})\left.\frac{\partial n}{\partial P}\right|_T$$

High temperature elasticity

(Wentzcovitch et al., PNAS 2009; Wu, Justo, and Wentzcovitch, PRL 2013)

$$V(P,T,n) = nV_{LS}(P,T) + (1-n)V_{HS}(P,T)$$

- **Compressibility:**

$$\frac{V(n)}{K(n)} = n\frac{V_{LS}}{K_{LS}} + (1-n)\frac{V_{HS}}{K_{HS}} - (V_{LS} - V_{HS})\frac{\partial n}{\partial P}\bigg|_T$$

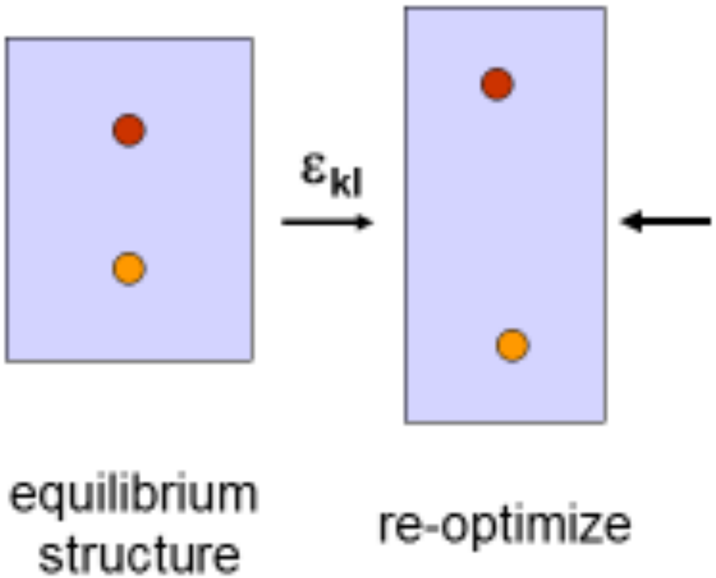
- **Compliances:**

$$S_{ij}(n)V(n) = nS_{ij}^{LS}V_{LS} + (1-n)S_{ij}^{HS}V_{HS} - \frac{1}{9}\alpha_{ij}(V_{LS} - V_{HS})\frac{\partial n}{\partial P}\bigg|_T$$

$$\alpha_{11} = \alpha_{12} = 1 \quad \alpha_{44} = 0$$

High Temperature Elastic Tensor

Karki et al., Science (1999), Wentzcovitch et al., PRL (2004)



$$c_{ij}^{T}(T,P) = \left[\frac{\partial^2 G}{\partial \varepsilon_i \partial \varepsilon_j}\right]_P$$

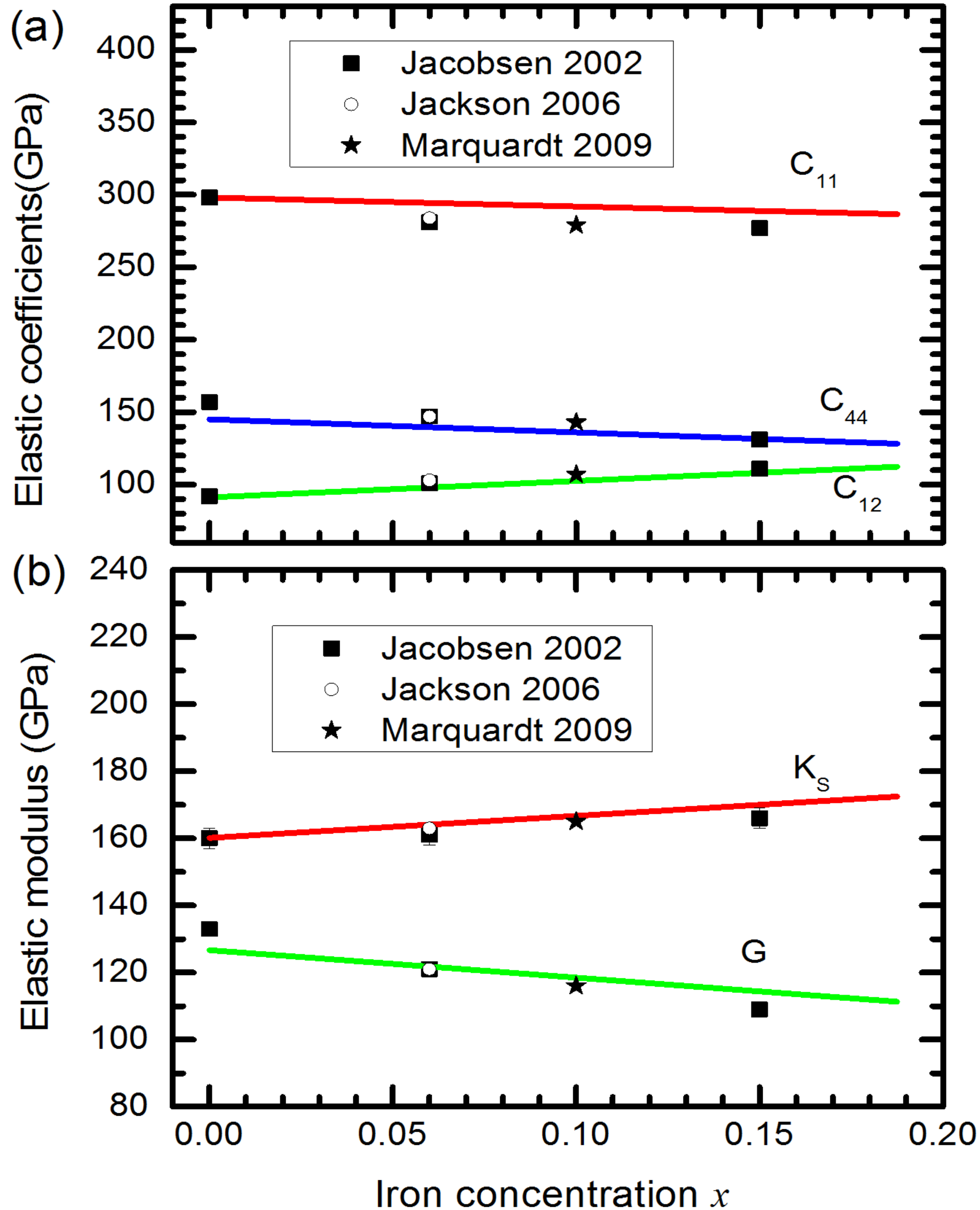
$$c_{ij}^{S}(T,P) = c_{ij}^{T}(T,P) + \frac{\lambda_i \lambda_j V T}{C_V}$$

$$\lambda_i = \left.\frac{\partial S}{\partial \varepsilon_i}\right|_T$$

10 volumes x 10 q-points x 10 strains = 1000 independent HPC tasks

High throughput calculations

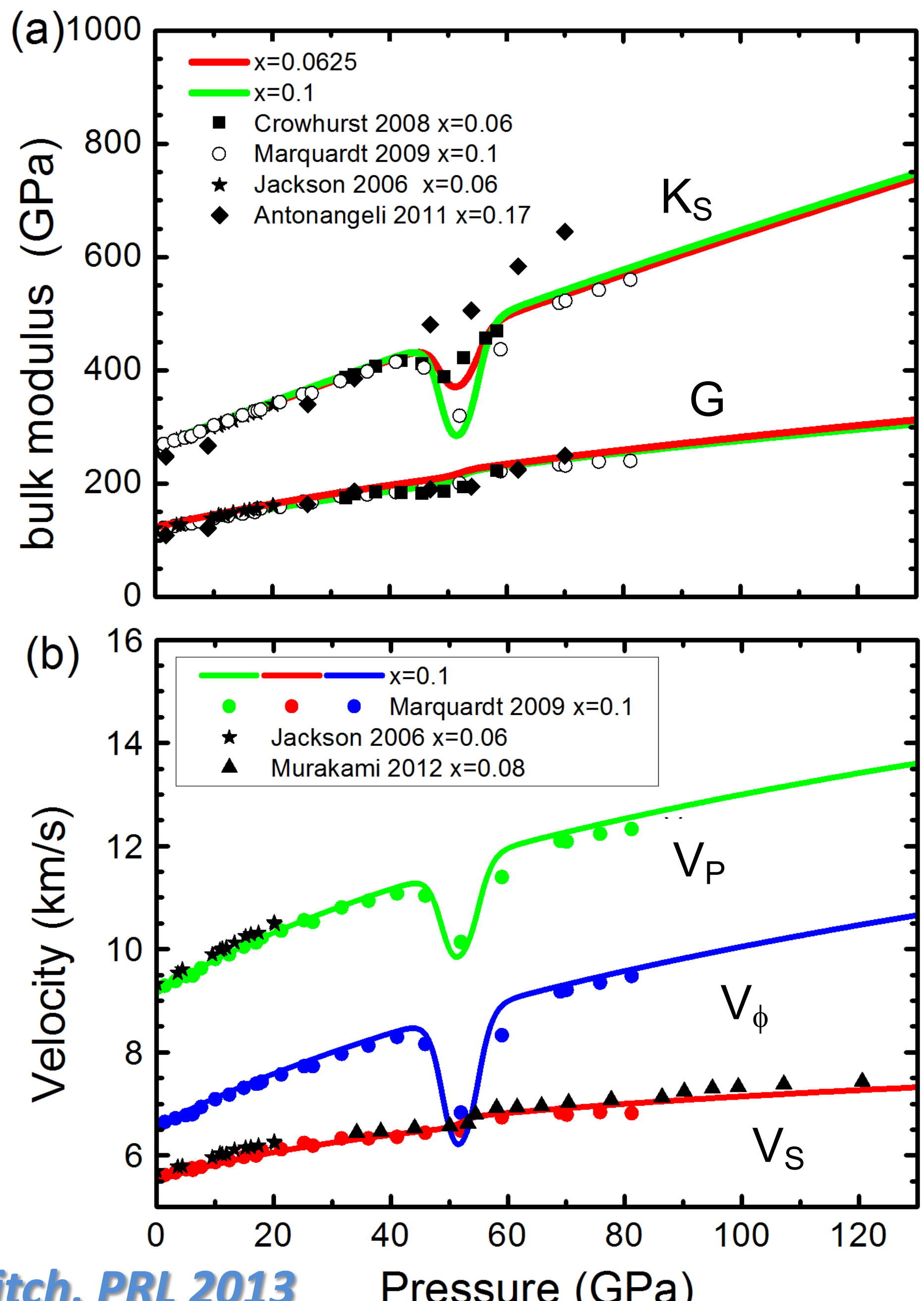
T = 300 K
P = 0 GPa



(a)
Elastic coefficients(GPa)
400
350
300
250
200
150
100
Jacobsen 2002
Jackson 2006
Marquardt 2009
C11
C44
C12
(b)
Elastic modulus (GPa)
240
220
200
180
160
140
120
100
80
Jacobsen 2002
Jackson 2006
Marquardt 2009
KS
G
0.00
0.05
0.10
0.15
0.20
Iron concentration x

Elastic anomalies in ferropericlase - I

T = 300 K



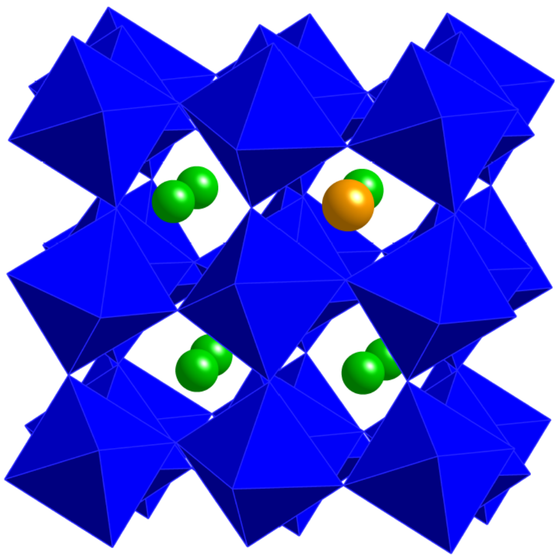
$$V_P = \sqrt{\frac{K_S + \frac{3}{4}G}{\rho}}$$

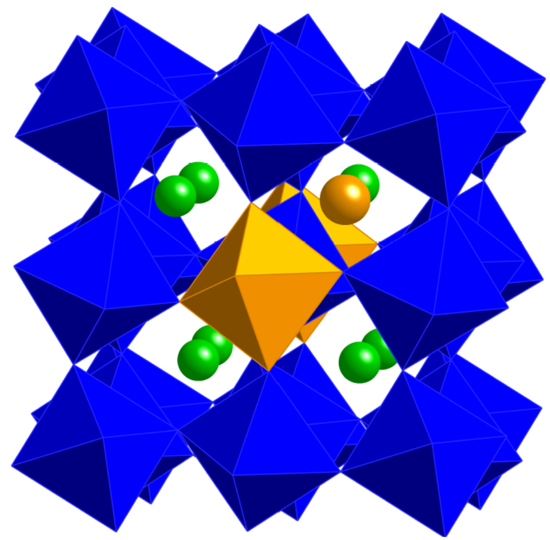
$$V_\phi = \sqrt{\frac{K_S}{\rho}}$$

$$V_S = \sqrt{\frac{G}{\rho}}$$

Wu, Justo, Wentzcovitch, PRL 2013

Spin Crossovers in bridgmanite





(Fe^{+2}) (Fe^{+3})

“New” species of Fe^{2+}: IS?

- At 0 GPa: HS state with QS = 2.4 mm/sec

- “New” Fe^{2+} (QS = 3.5 mm/s) for *P* > 30 GPa

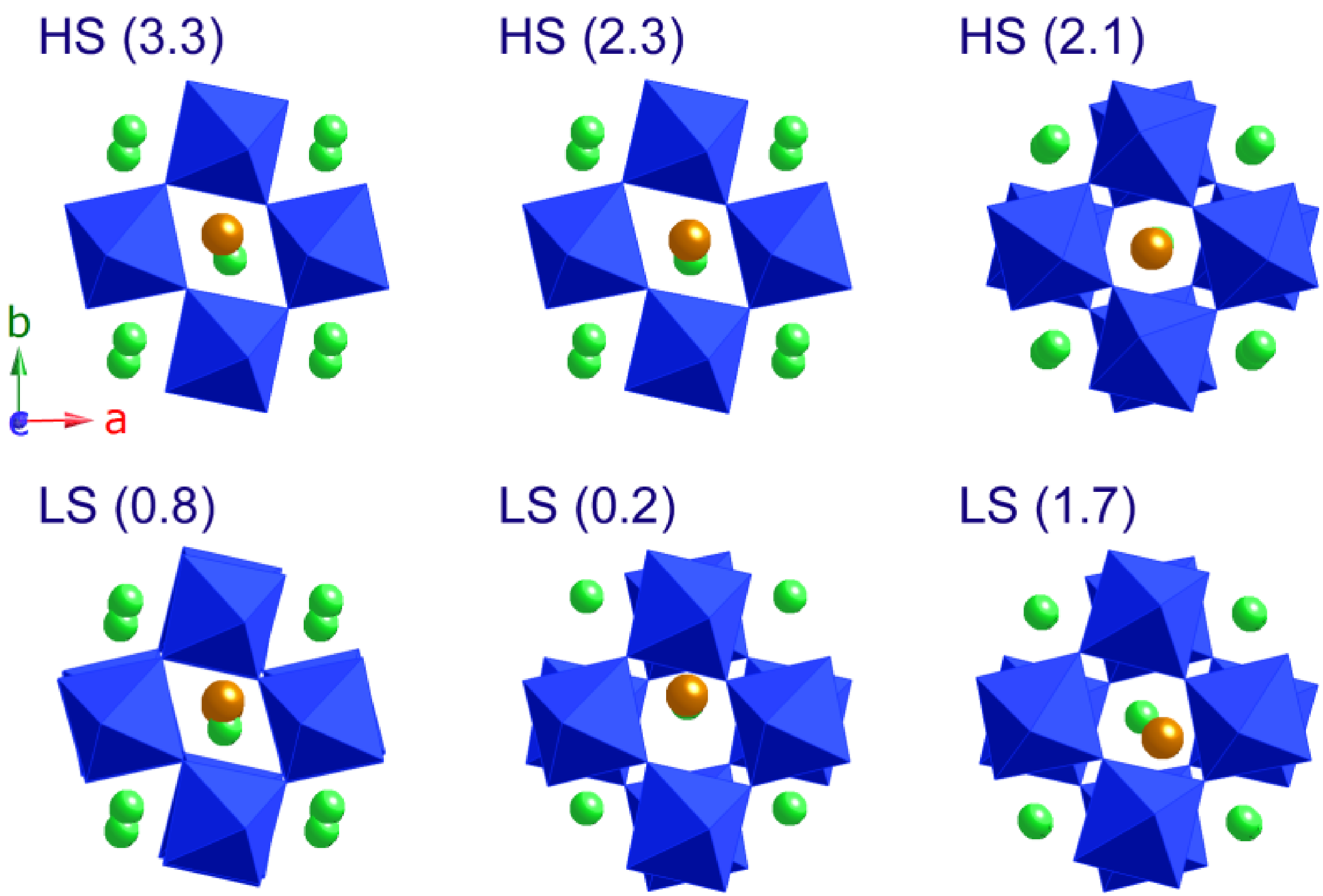
- Fe^{2+} QS = 3.5 mm/s increases at the expense of the HS Fe^{2+} (QS = 2.4 mm/s)

- The two sets of peaks “merge” at P ~ 60 GPa

McCammon et al. Nature Geoscience (2008)

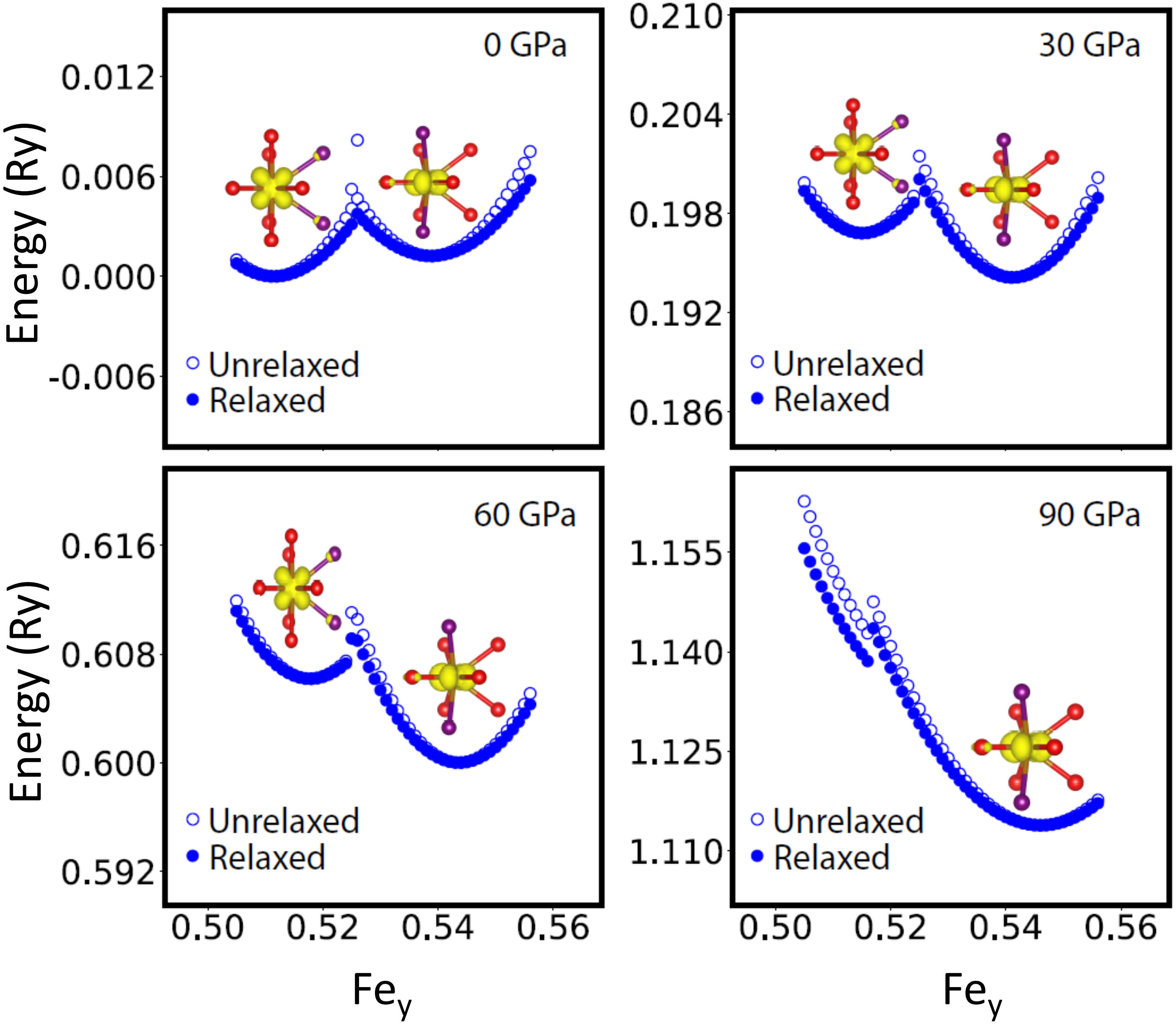
HS and LS configurations at 0 GPa

x_{Fe} = 0.25 and 0.125



Hsu, Umemoto, Blaha, and Wentzcovitch, EPSL 2009

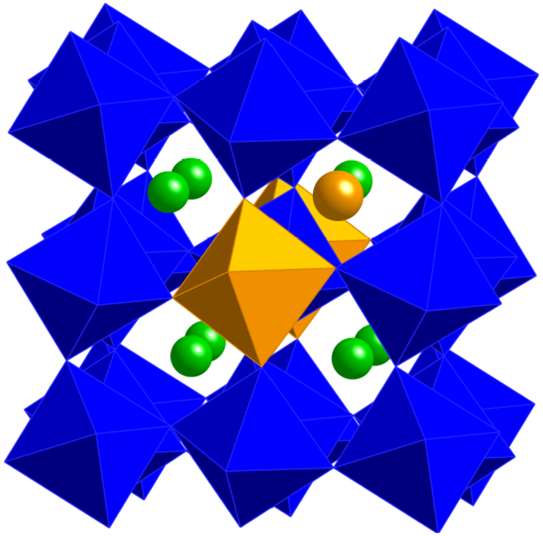
The double-well with LDA+U_{sc}



- $(Mg_{0.875}Fe_{0.125})SiO_3$
- **No spin crossover**

Lacerda et al., 2018

Spin Crossover in Perovskite



(Fe^{+3})

What we know:

Experiments

XES	HS → LS (P_T ~ 50-60 GPa)
Mössbauer (QS: ~0.5 → ~3.0 mm/s)	50% HS → LS 50% remains HS (P_T ~ 150 GPa)

Catalli *et al*.,
EPSL (2010)

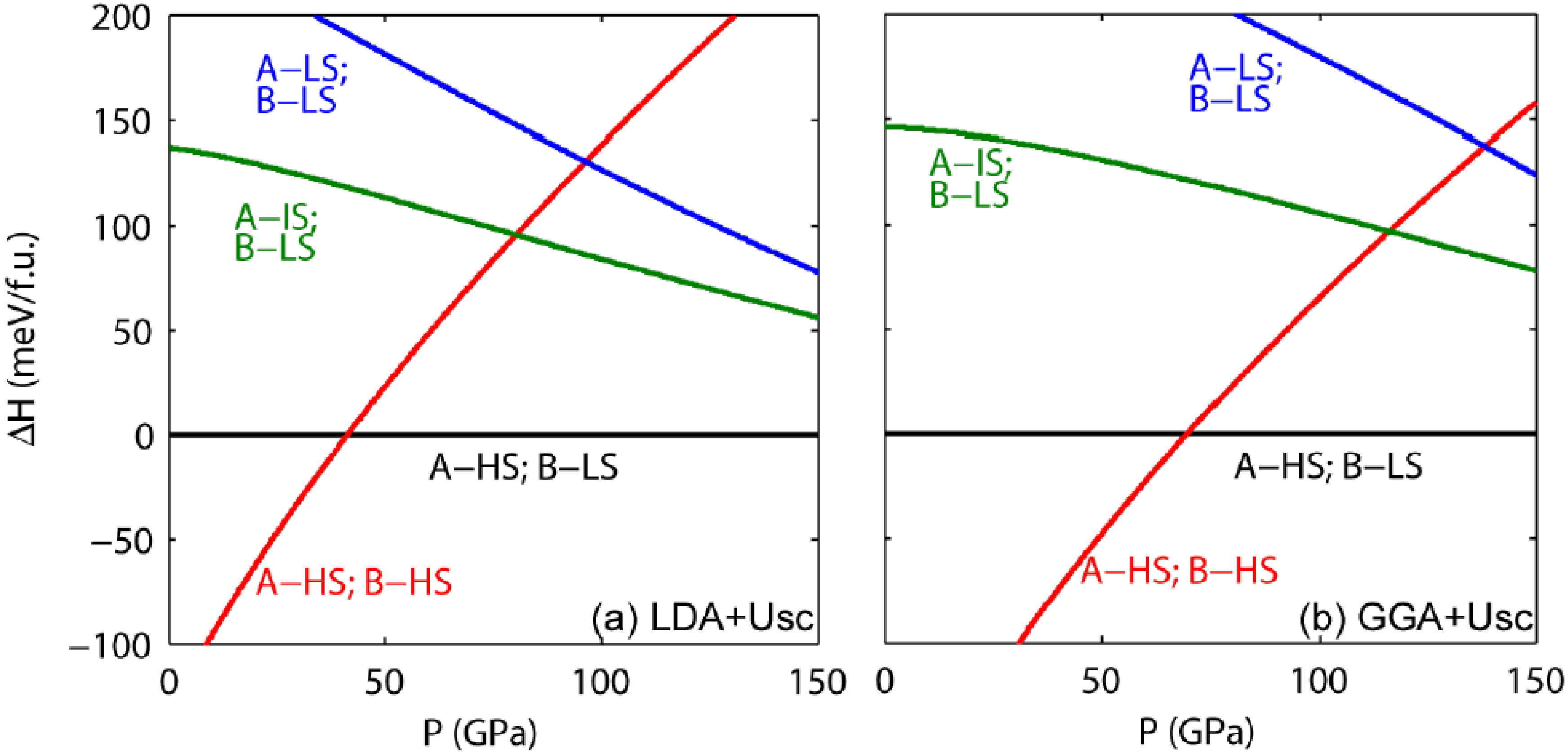
Calculations

GGA	Ground state: (A-HS, B-LS) (A-HS, B-LS) → (A-LS, B-LS) P_T > 75 GPa Zhang & Oganov, EPSL (2006) Stackhouse *et al*., EPSL (2007)

Inconsistent with Exp
- P_T too high
- Fraction of HS Fe^{3+} too low

Relative Enthalpies (U_{SC})

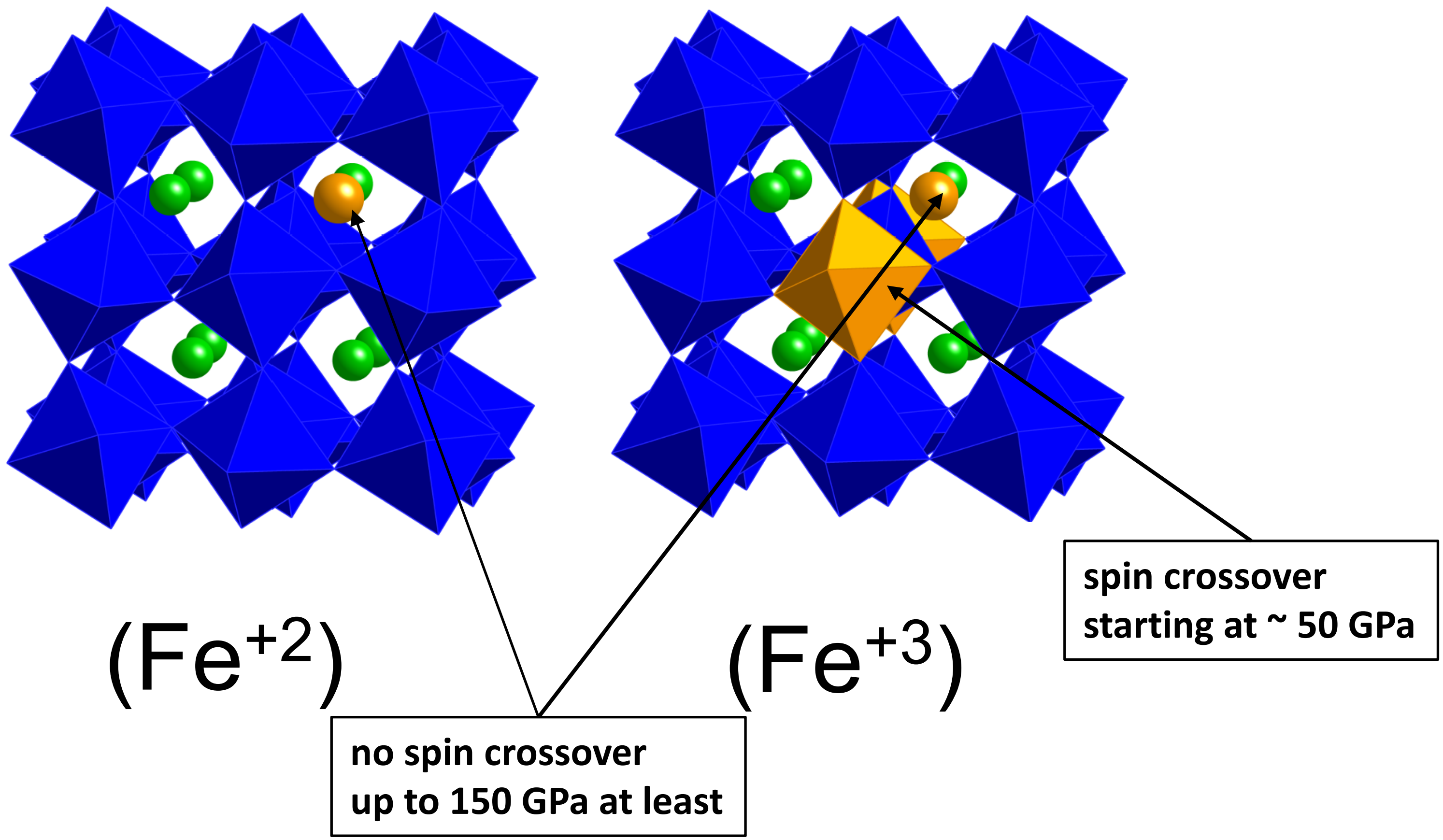
LDA+U_{SC} P_T= 41 GPa GGA+U_{SC} P_T= 70 GPa



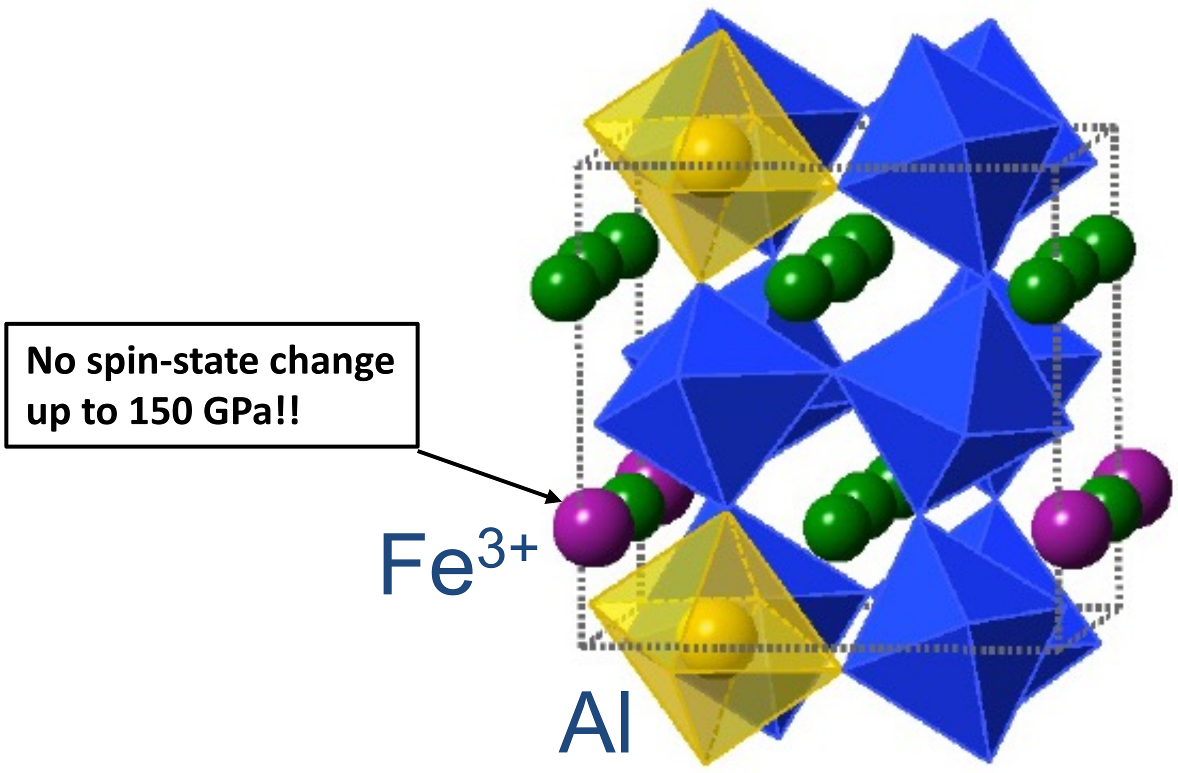
P_T observed in XES: 50-60 GPa

Hsu *et al.*, PRL (2011)

Spin Crossovers in bridgmanite

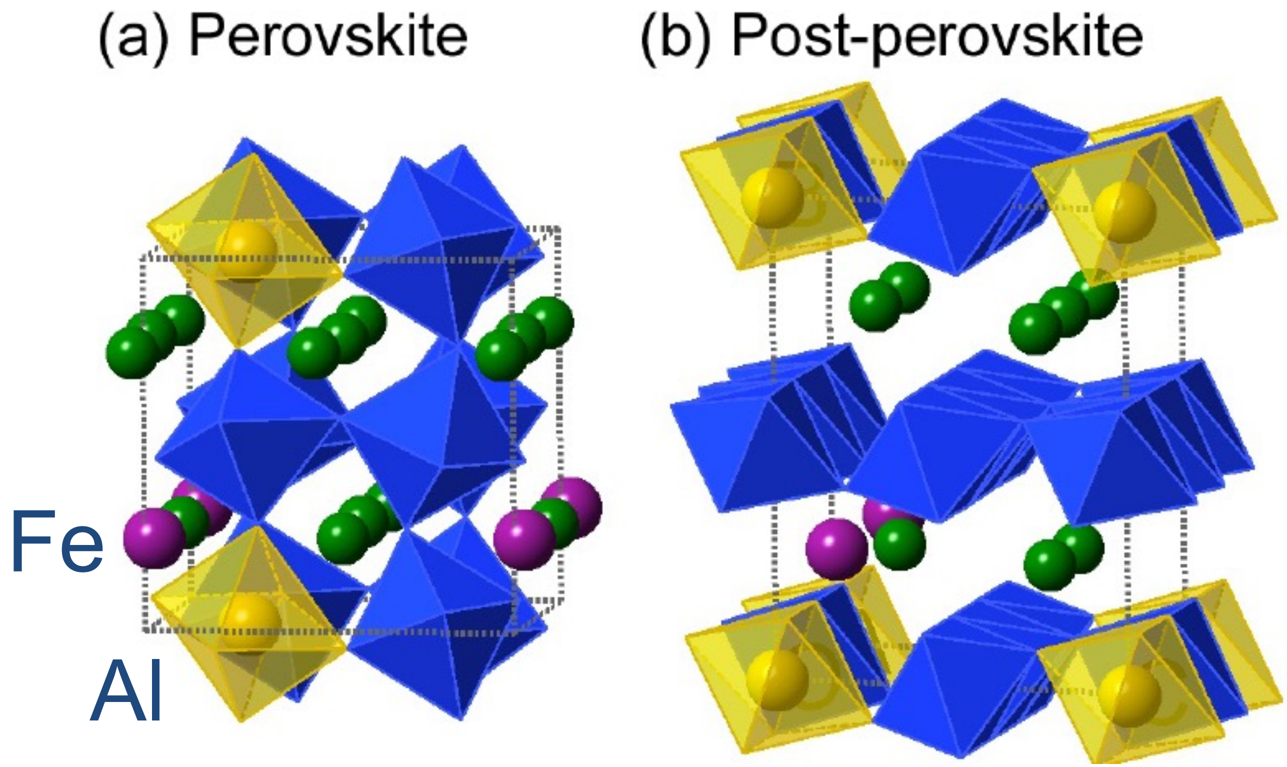


Spin crossover in aluminous Pv



Hsu, Yu, and Wentzcovitch (EPSL 2012)

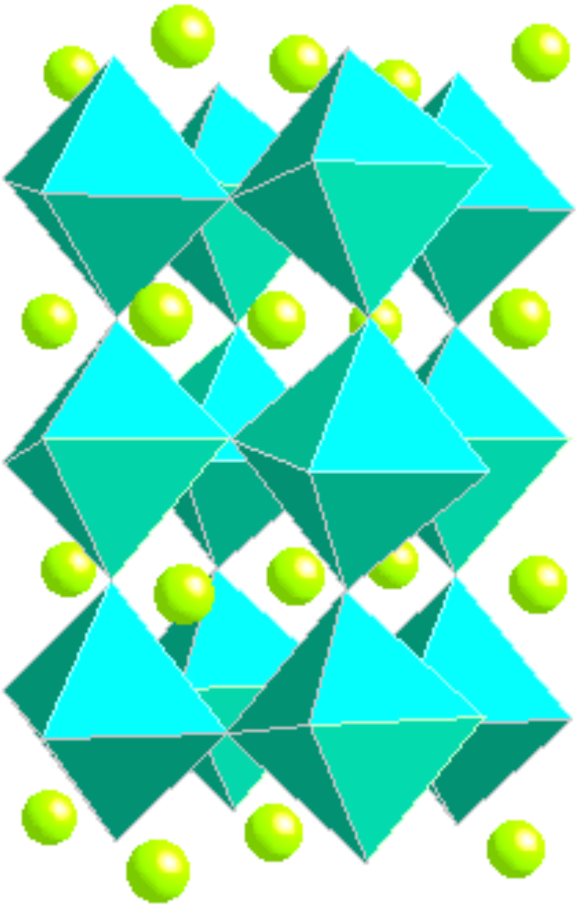
Spin crossover in aluminous Pv and PPv



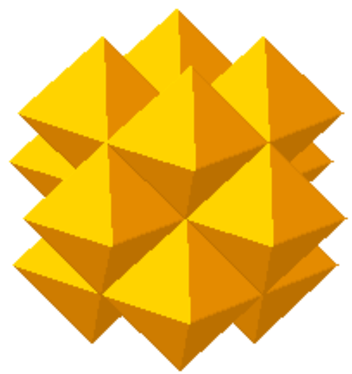
Hsu, Yu, and Wentzcovitch (EPSL 2012)

Consequences for Mantle Structure

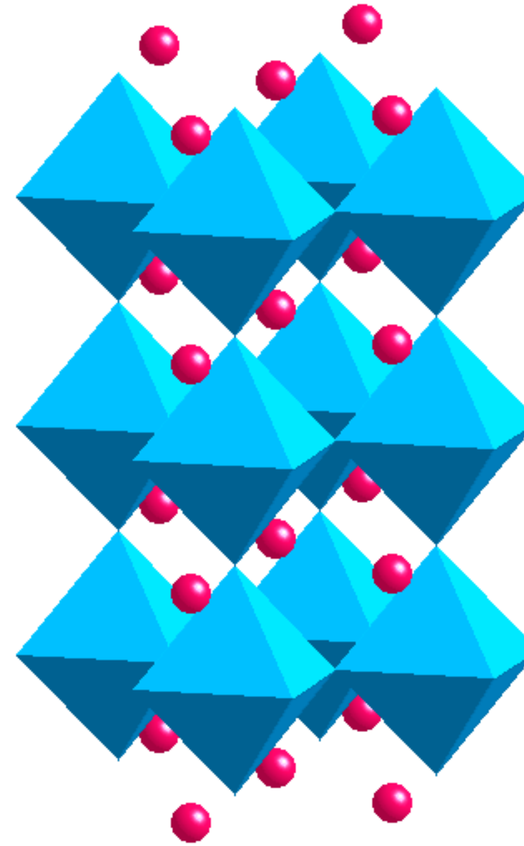
Lower Mantle



+



+



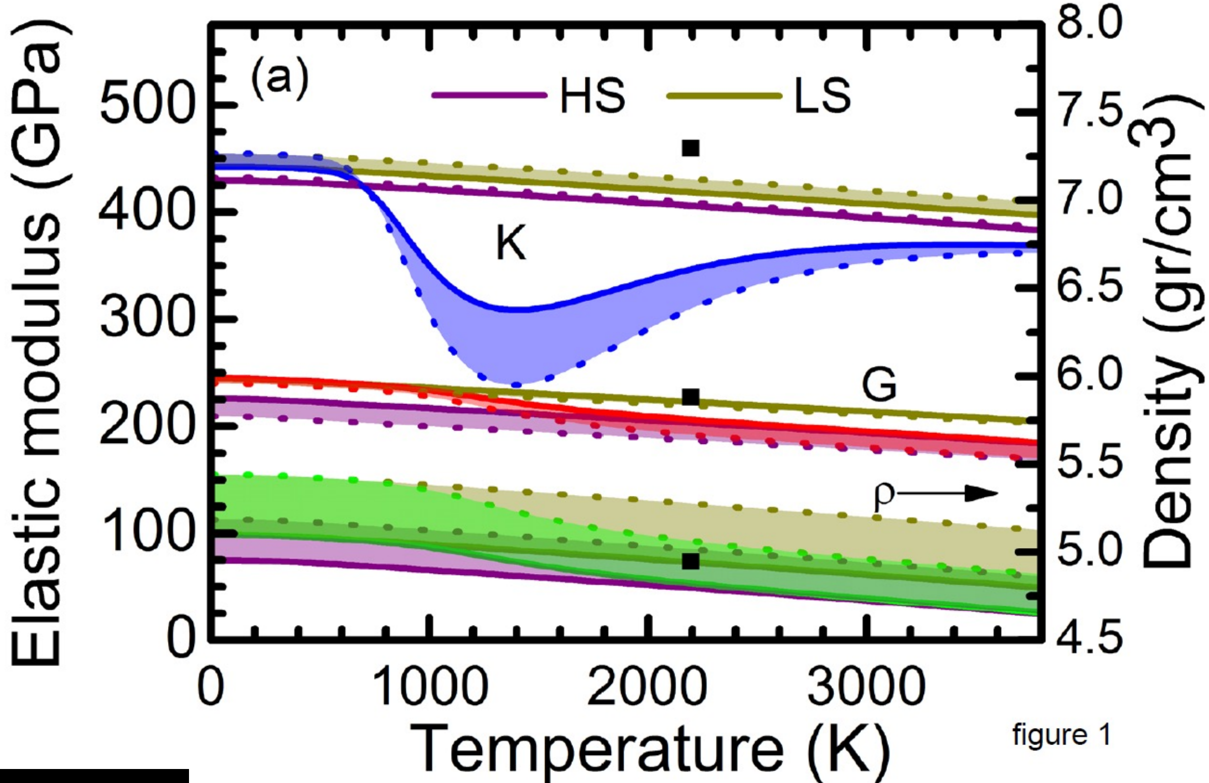
$(Mg_{(1-x-z)},Fe_x, Al_z)(Si_{(1-y)},Al_y)O_3$

$(Mg_x,Fe_{(1-x)})O$

$CaSiO_3$

Elastic anomalies in ferropericlase - II

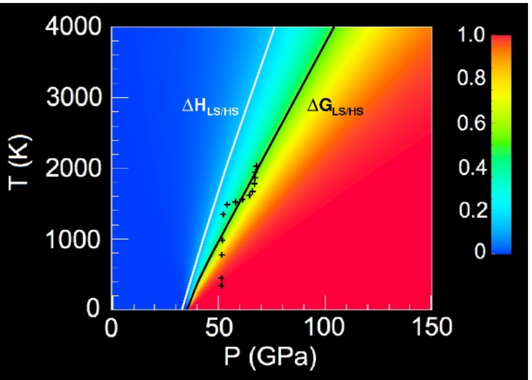
Wu and Wentzcovitch, PNAS 2014



P = 75 GPa

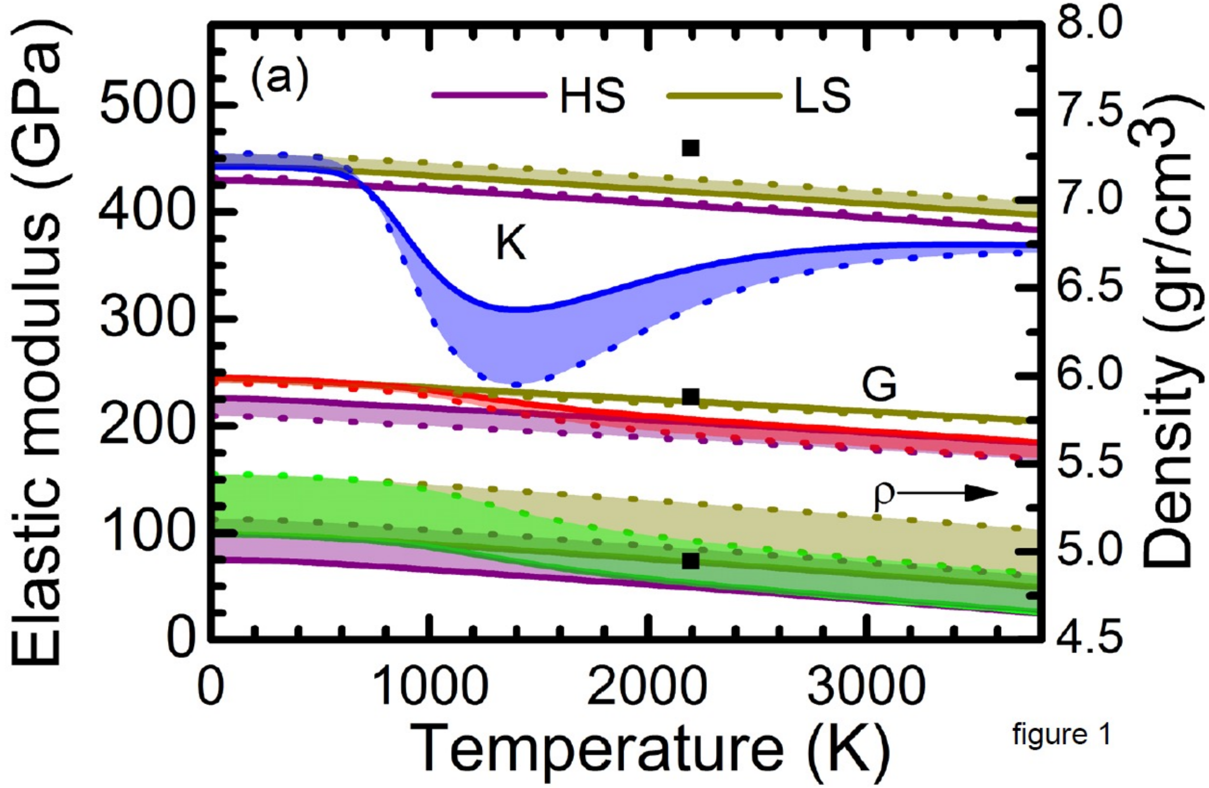
—— $Mg_{0.88}Fe_{0.12}O$

- - - $Mg_{0.79}Fe_{0.21}O$



Elastic anomalies in ferropericlase - II

Wu and Wentzcovitch, PNAS 2014



P = 75 GPa

—— $Mg_{0.88}Fe_{0.12}O$

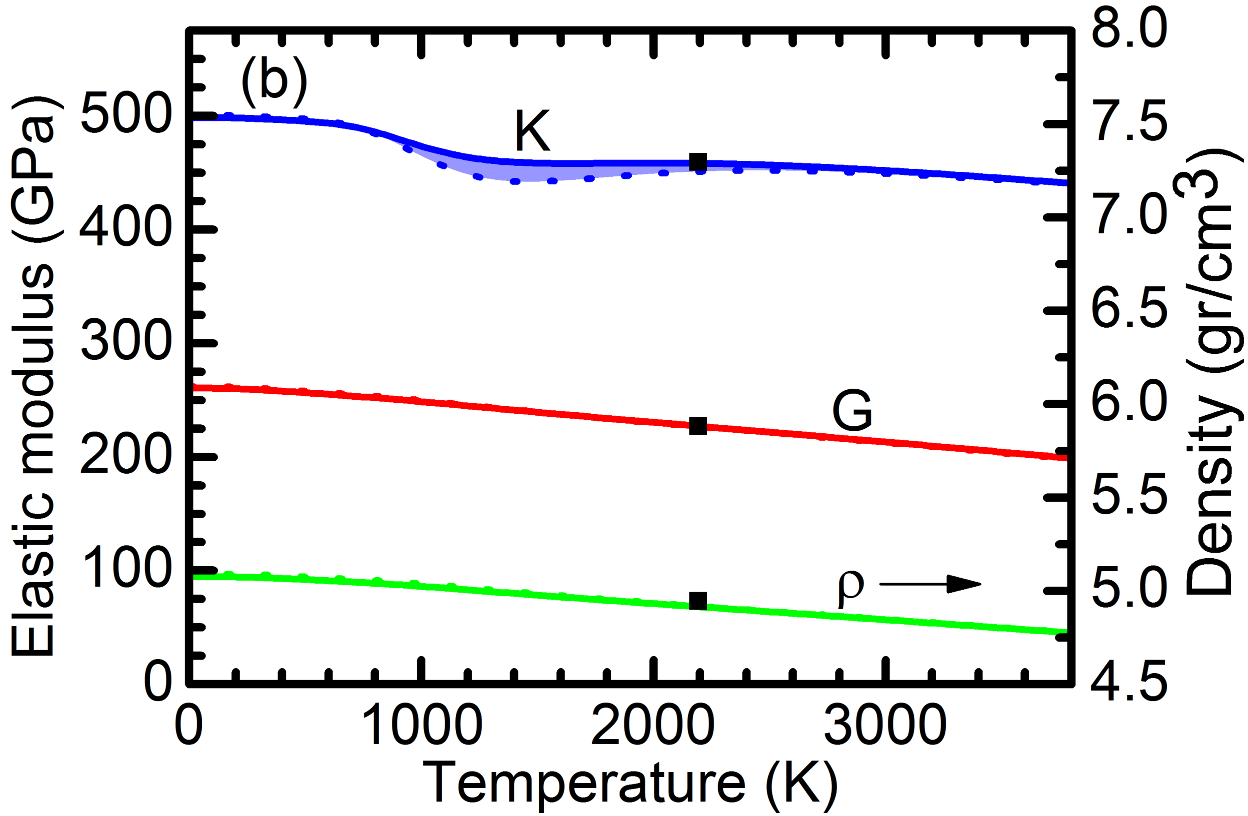
- - - $Mg_{0.79}Fe_{0.21}O$

$$V_P = \sqrt{\frac{K_S + \frac{3}{4}G}{\rho}}$$

$$V_S = \sqrt{\frac{G}{\rho}}$$

Lower mantle aggregate

Wu and Wentzcovitch, PNAS 2014



P = 75 GPa

—— 78% $(Mg_{0.91}Fe_{0.09})SiO_3$ (MgPv) + 7% $CaSiO_3$ + 15% $Mg_{0.88}Fe_{0.12}O$

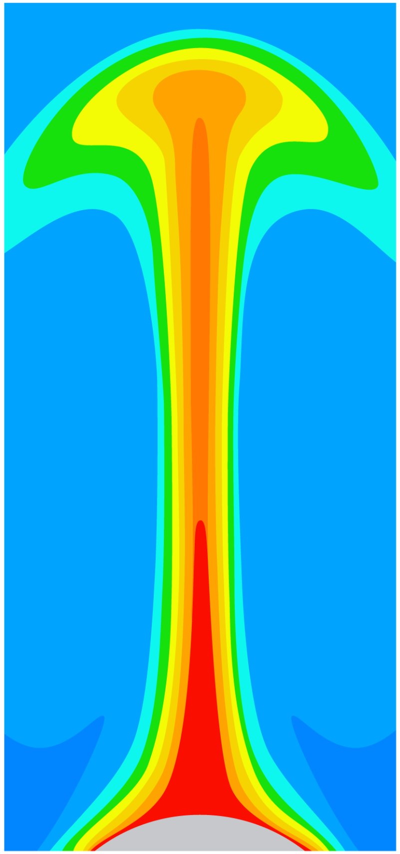
- - - 78% $(Mg_{0.91}Fe_{0.09})SiO_3$ (MgPv) + 7% $CaSiO_3$ + 15% $Mg_{0.79}Fe_{0.21}O$

Predicted effect

Wu and Wentzcovitch, PNAS 2014

<u>Slow (hot) anomaly (plume) with spin crossover</u>

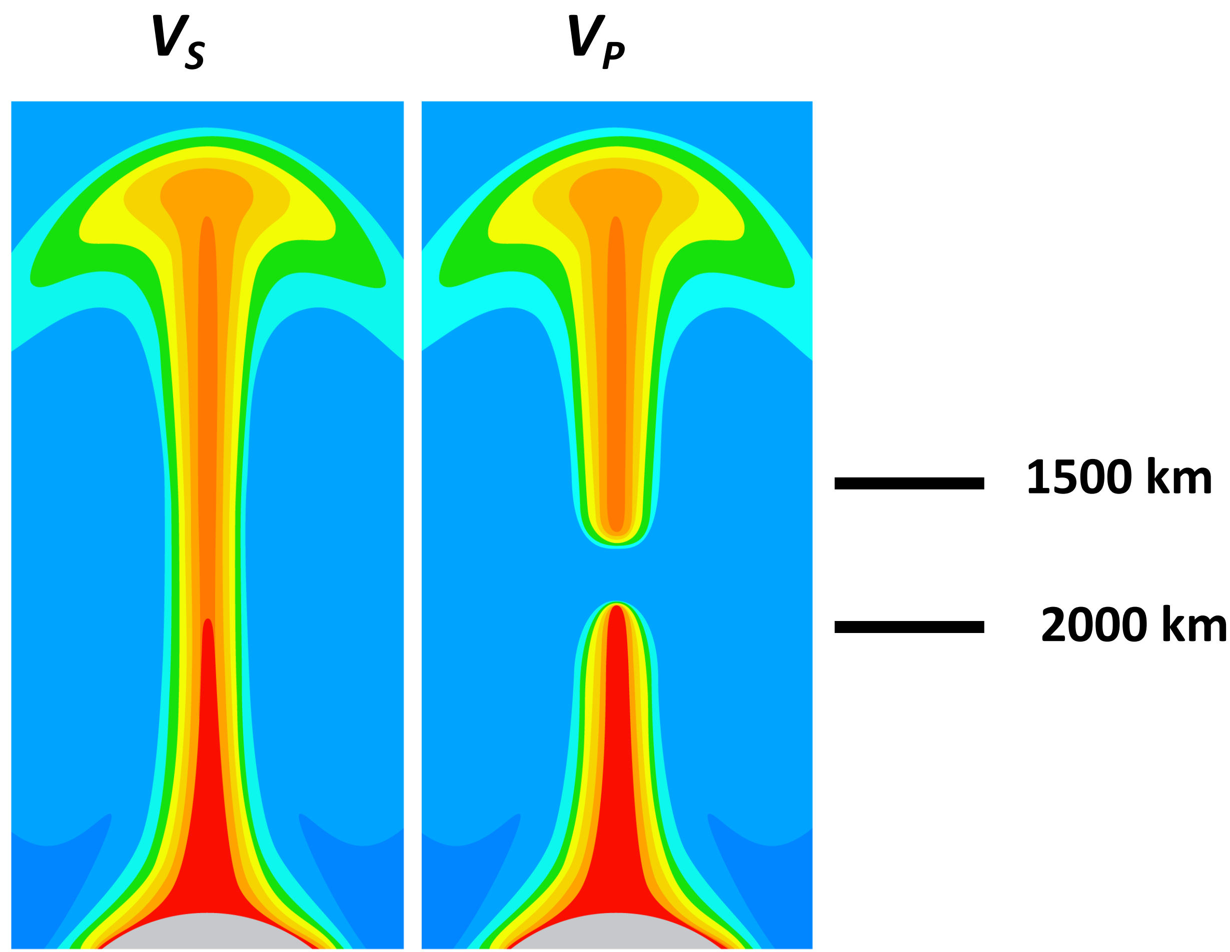
V_S



Predicted effect

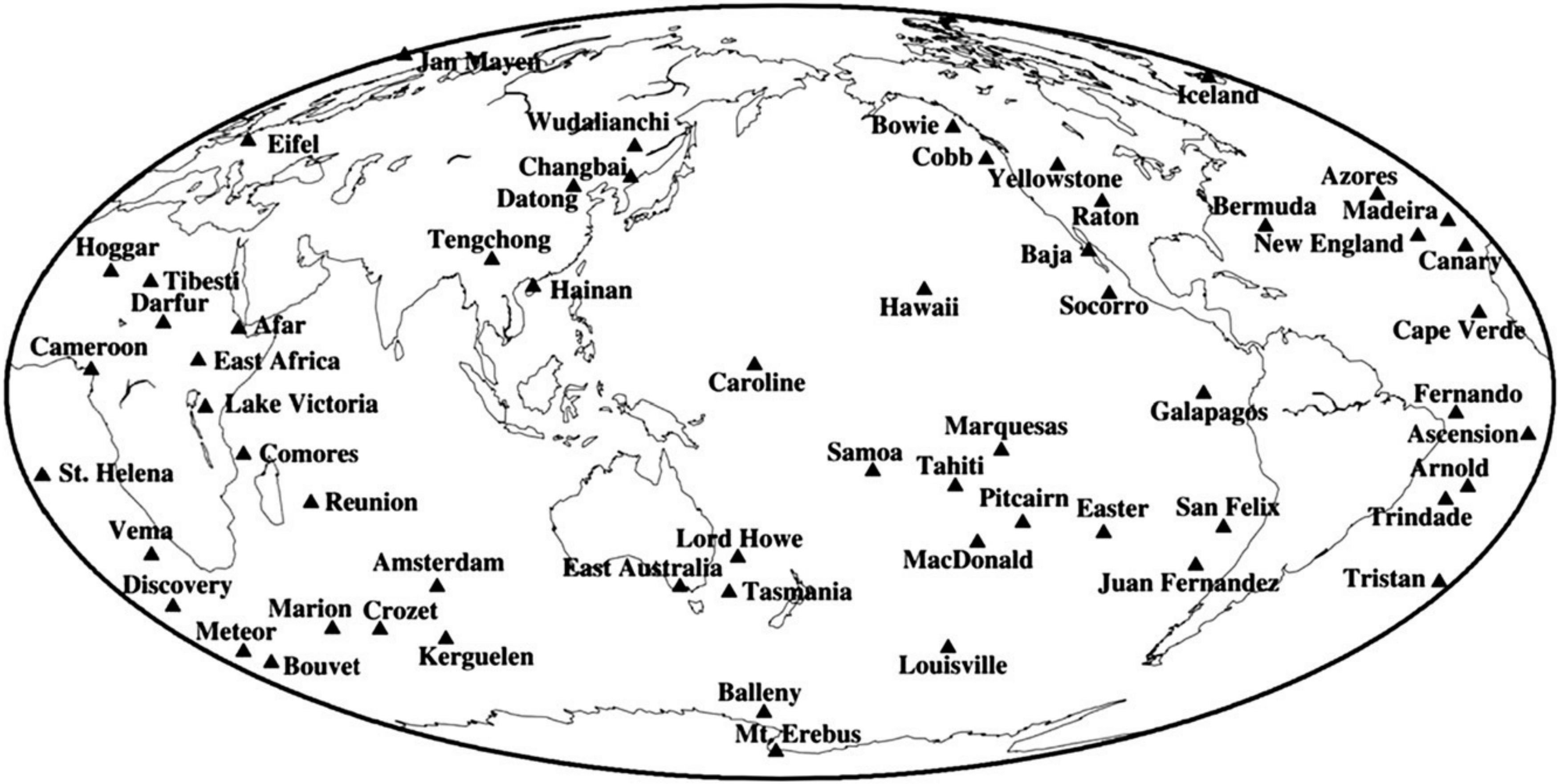
Wu and Wentzcovitch, PNAS 2014

Slow (hot) anomaly (plume) with spin crossover



Potential seismic signatures of spin crossover

Wu and Wentzcovitch, PNAS 2014

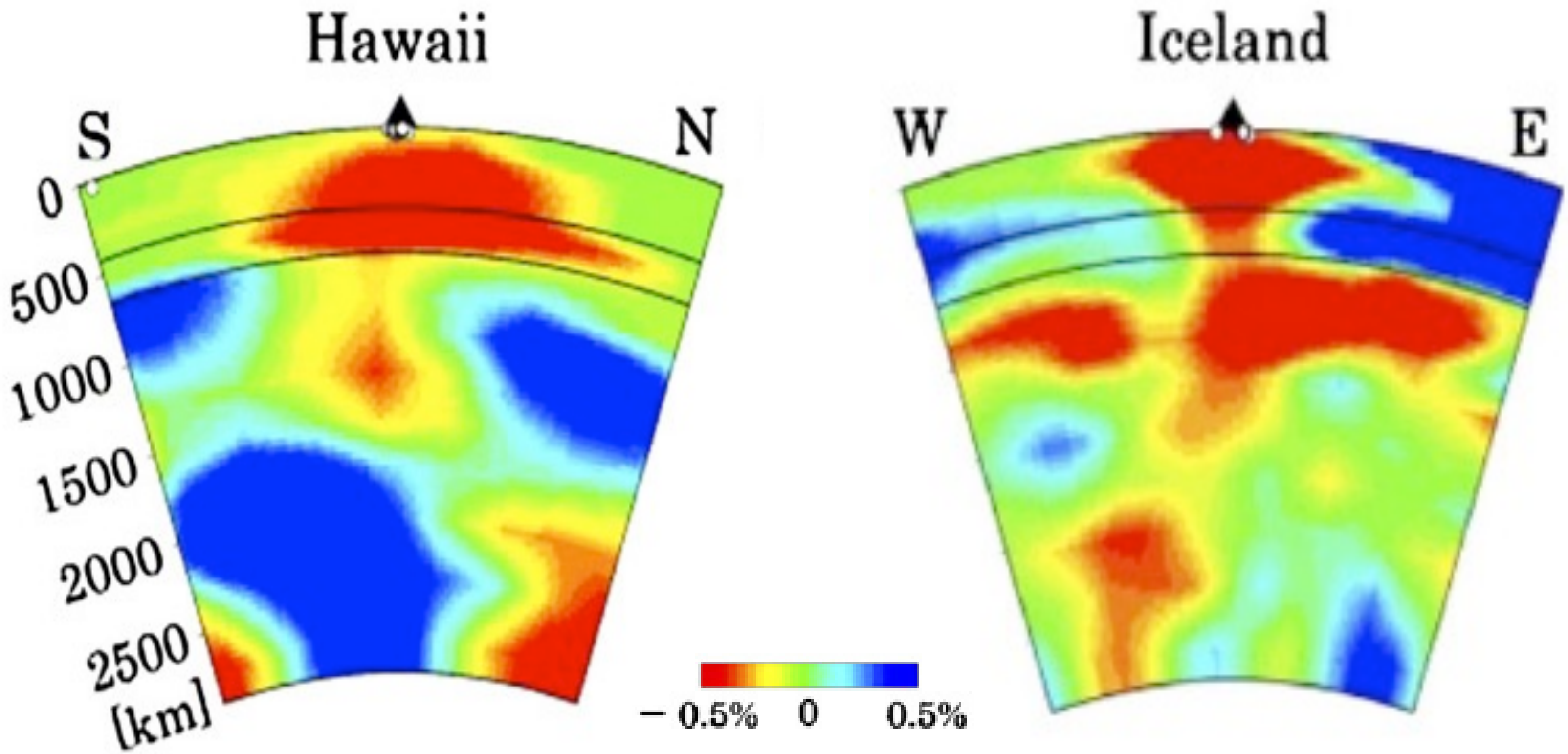


Zhao, Gondwana Res. 2007

P-models

Potential seismic signatures of a spin crossover

Wu and Wentzcovitch, PNAS 2014

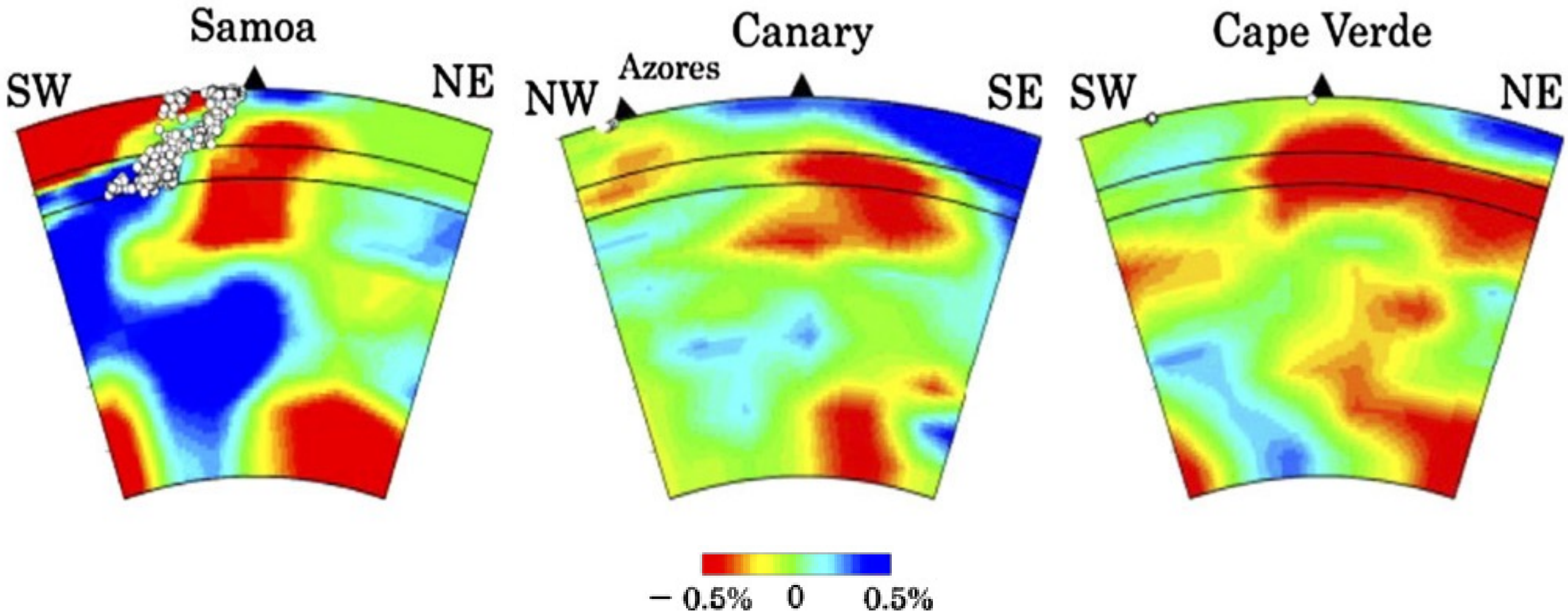


Zhao, Gondwana Res. 2007

P-models

Potential seismic signatures of spin crossover

Wu and Wentzcovitch, PNAS 2014



Zhao, Gondwana Res. 2007

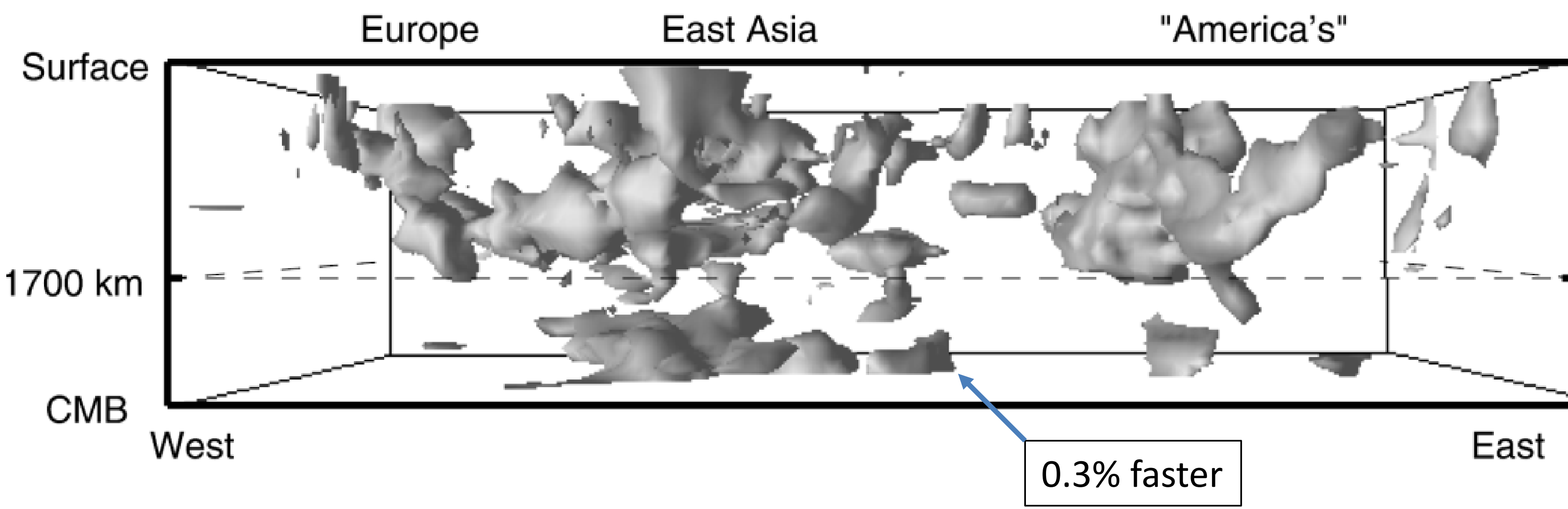
P-models

Compositional Heterogeneity in the Bottom 1000 Kilometers of Earth's Mantle: Toward a Hybrid Convection Model

Science AAAS

1999

Rob D. van der Hilst* and Hrafnkell Kárason

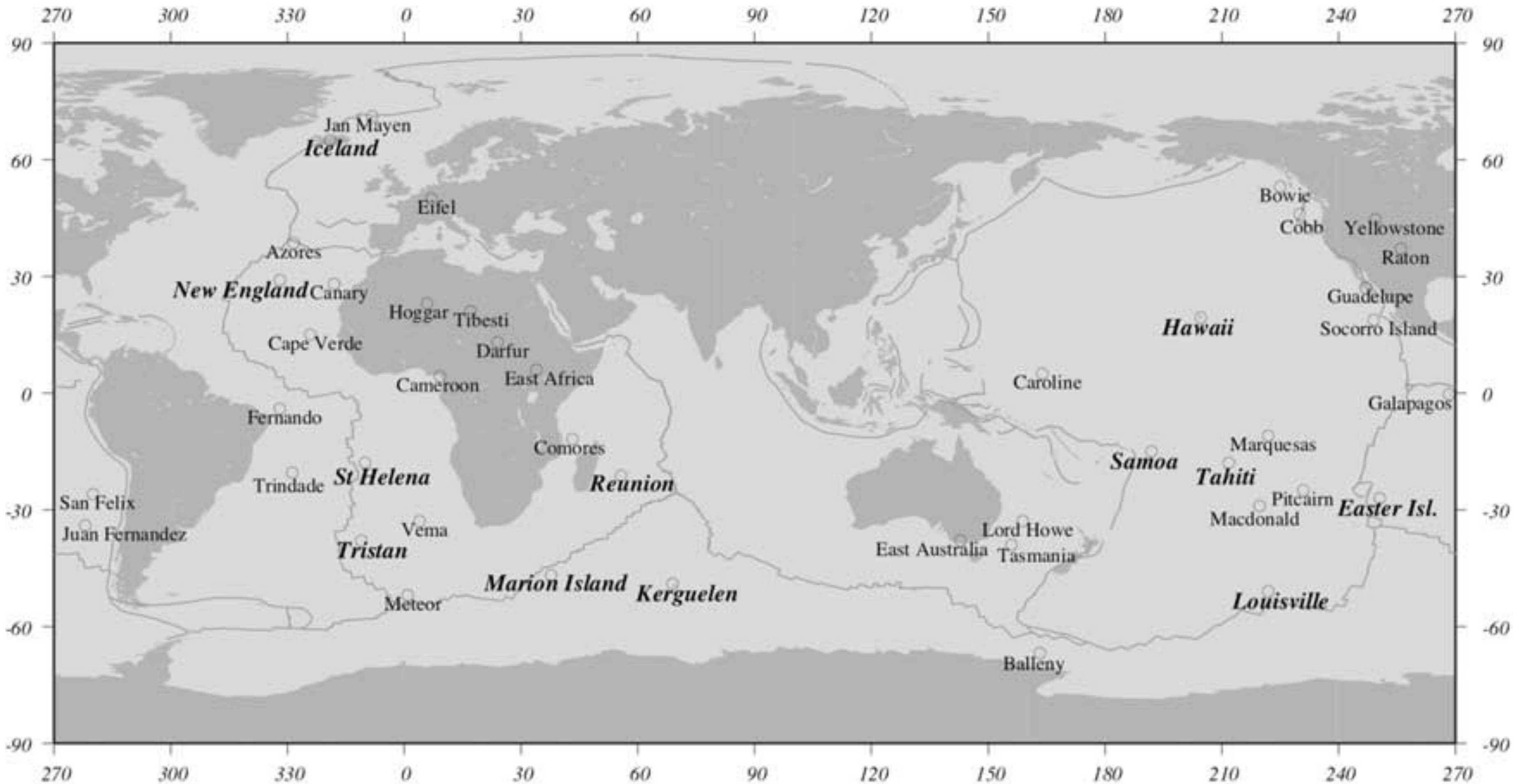


P-model

Geodynamic/seismological analysis of global models

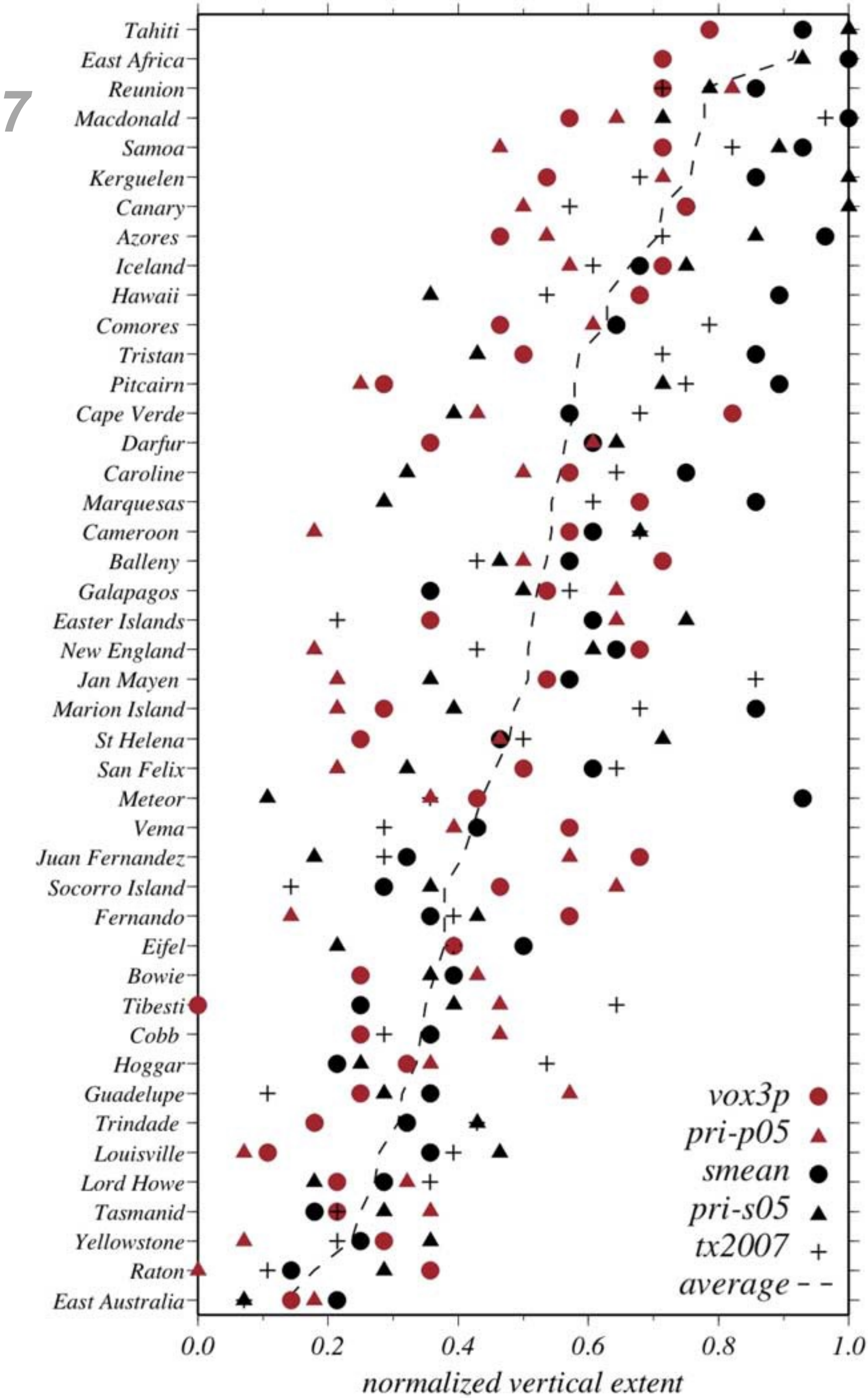
Boschi, Becker, Steinberger, G³, 2007

Simultaneous analyses of 2 global P-models and 3 global S-models



Boschi, Becker, Steinberger, G³, 2007

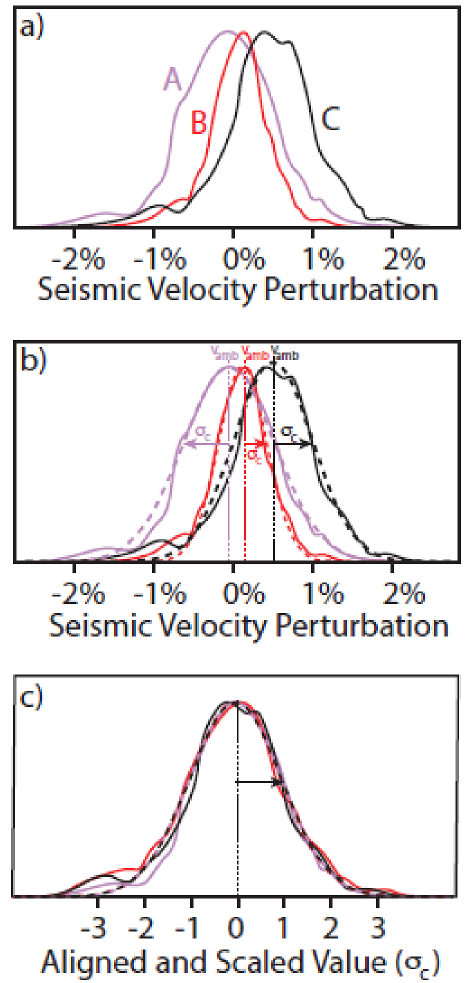
- **Tomographic S-models can identify ~ 10 continuous slow/hot conduits extending from CMB to surface (plumes), while P-models do not identify a single one!**



Can we see the spin transition in the lower mantle? NOT IN PREM but perhaps in ak135!
How do tomographic models compare? “VOTE MAPS”

<u>4 S-models</u>:
- **HMSL-S06** (*Houser, Masters, et al. 2006*)
- **S40RTS** (*Ritsema et al., 2011*)
- **SEMUCB-WM1** (*French & Romanowicz, 2014*)
- **savani** (*Auer, Boschi, Becker et al., 2014*)

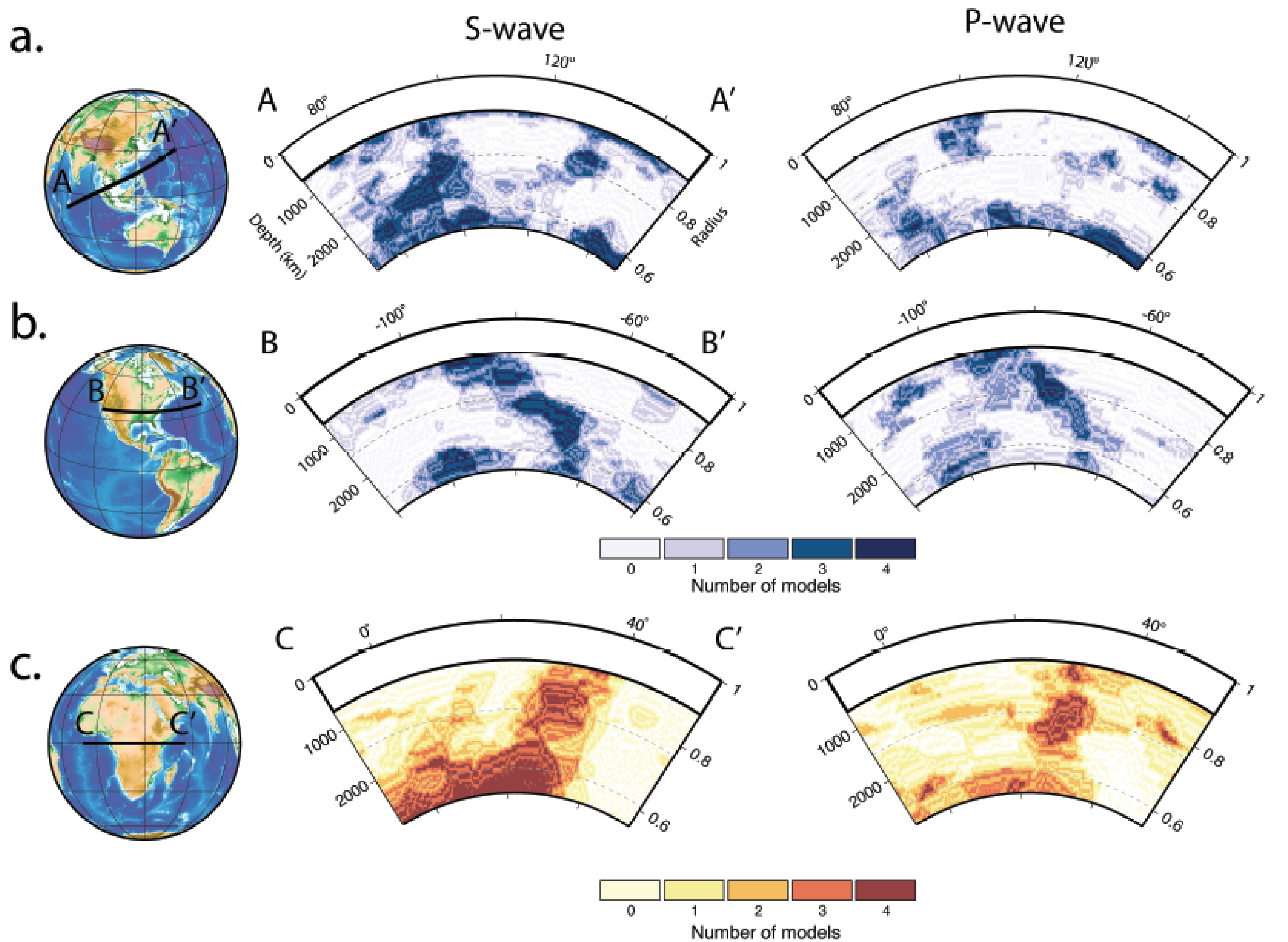
<u>4 P-models</u>:
- **HMSL-P01** (*Houser, Masters, et al. 2006*)
- **DETOX-P01** (*Hoseini & Sigloch, 2011*)
- **GAP-P4** (*Obayashi, Fukao, 2013*)
- **MITP-2011** (*Burdick et al., 2011*)



How many models have ΔV> +1σ or ΔV<-1 σ?

Shephard, Hernlund, Houser, Tronnes, Valencia-Cardona, Wentzcovitch, Nature Communications, in press (2021)

Can we see the spin crossover in the lower mantle?
How do tomographic models compare? "VOTE MAPS"



Shepard, Hernlund, Houser, Tronnes, Valencia-Cardona, Wentzcovitch, Nature Communications (2021)

Summary:

- Iron spin crossover (ISC) is not an obvious global feature (1d profile)
- Significant in the fast anomaly (slab) regions from 1,500km – 2,000km depth -- Effect of Temperature + Composition(?)
- Observable in the slow anomaly (plume) regions from 1,800km to 2,200km depth. Yet, not as strong as slab regions.
- All these observations requires high-resolution tomographic models.

Future Work:

- GLAD-M35:
- Further modeling for temperatures, pressures, and composition in the lower mantle
- Extract mineralogical and temperature information directly from GLAD-M35

Some Challenges

- ANHARMONIC EFFECTS: temperature dependent phonon frequencies, thermal conductivity, anharmonic free energy, pre-melting behavior, etc…

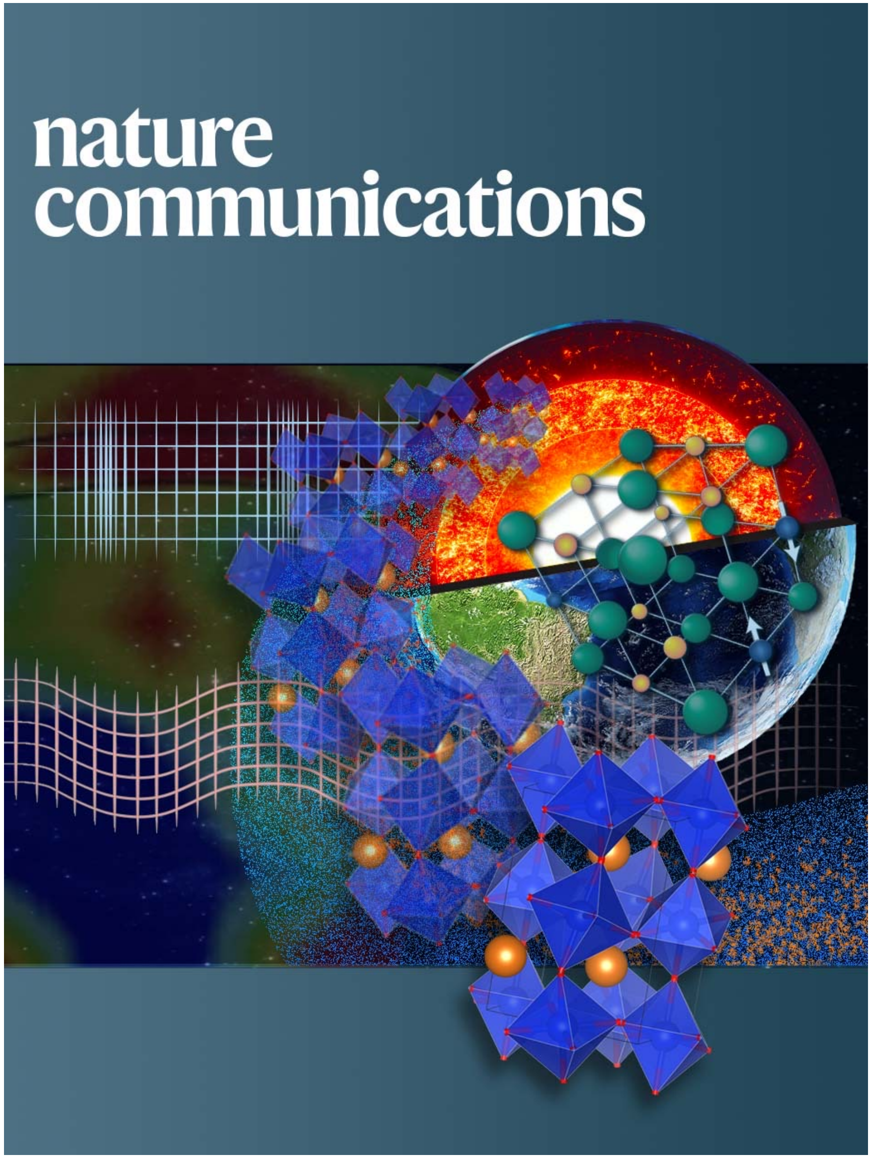
- SEARCH FOR new phases, particularly with high iron content

- MULTI-PHASE EQUILIBRIUM: address co-existing complex solid solutions (more accurate free energies).

Acknowledgments

- Koichiro Umemoto (ELSI, Tokyo)
- Wenjie Lei (Google)
- Matteo Cococcioni (EPFL, Lausanne)
- Stefano de Gironcoli (SISSA, Trieste)
- Gaurav Shukla (IIT-Kolkata)
- João F. Justo (USP, São Paulo, Brazil)
- Zhongqing Wu (USTC, Hefei)
- Juan Valencia-Cardona (Intel)
- Han Hsu (Taiwan Central University)
- Taku and Jun Tsuchiya (Ehime, Japan)
- Peter Blaha (Vienna, Austria)
- Maribel Núnez-Valdéz (Potsdam, Germany)
- Yonggang Yu (NOAA, USA)
- Pedro da Silveira (Apple Inc.)
- Jingyi Zhuang (Columbia University)

Spin crossover in the lower mantle



Shepard, Hernlund, Houser, Tronnes, Valencia-Cardona, Wentzcovitch, Nature Communications, (2021)