Spin crossovers in iron bearing minerals of the lower mantle

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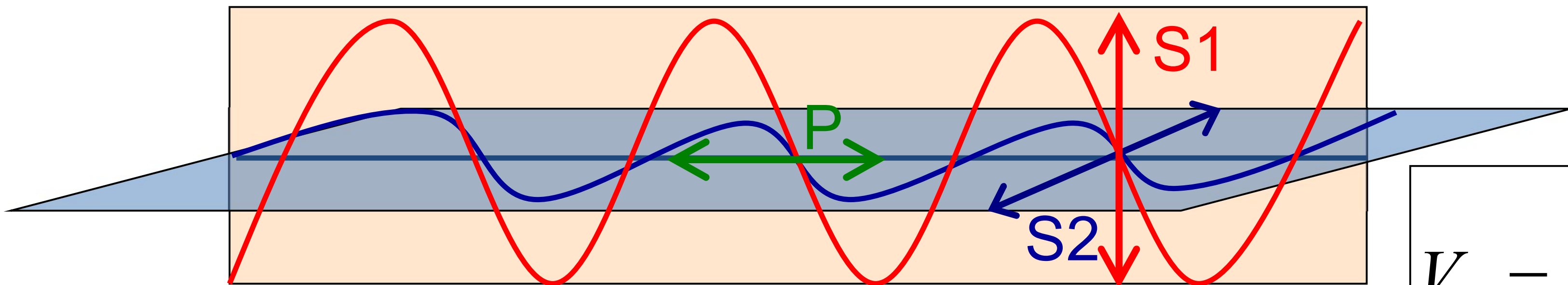
Body wave (acoustic) velocities

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

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

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

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



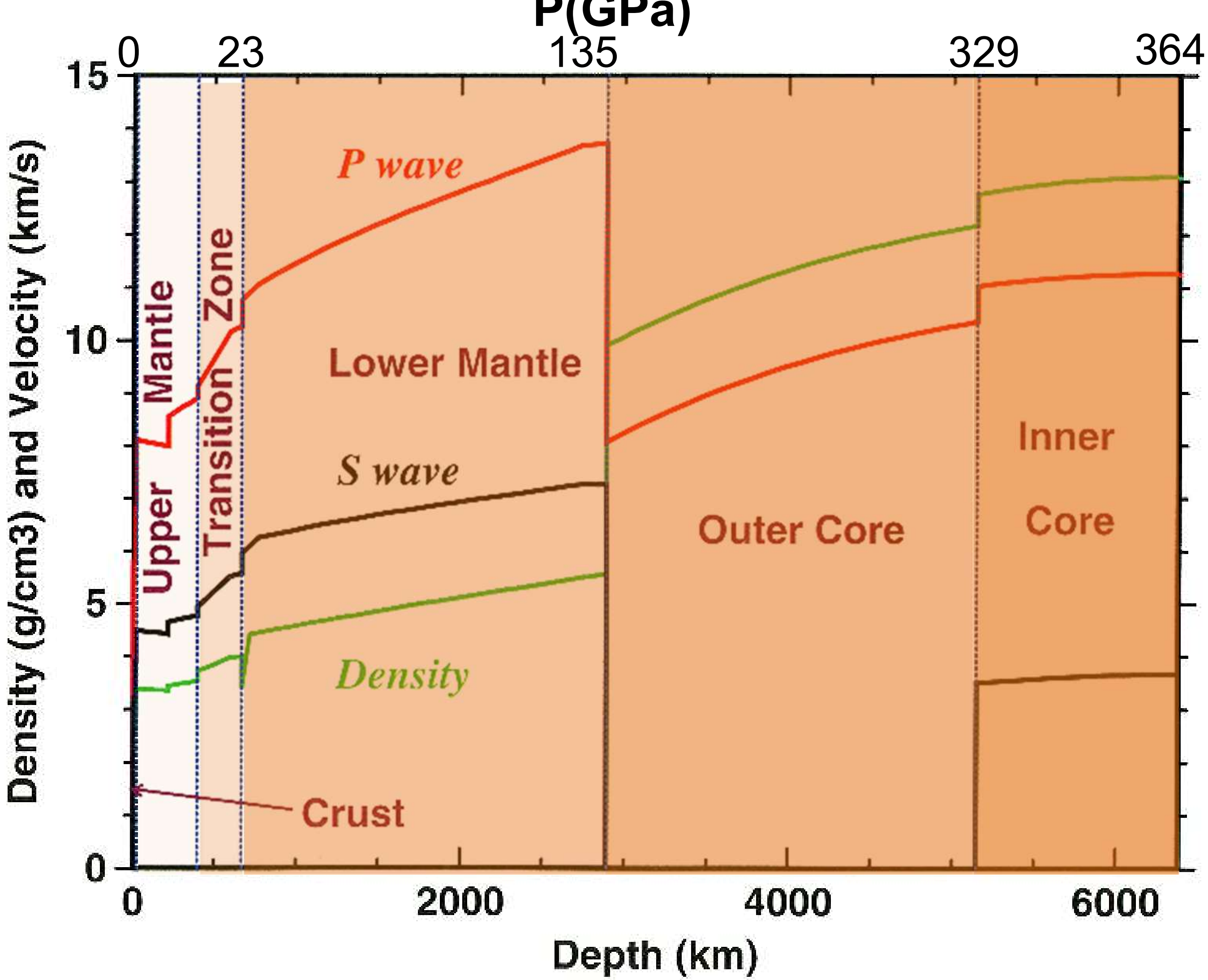
$$V_\varphi = \sqrt{\frac{K}{\rho}}$$

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

PREM

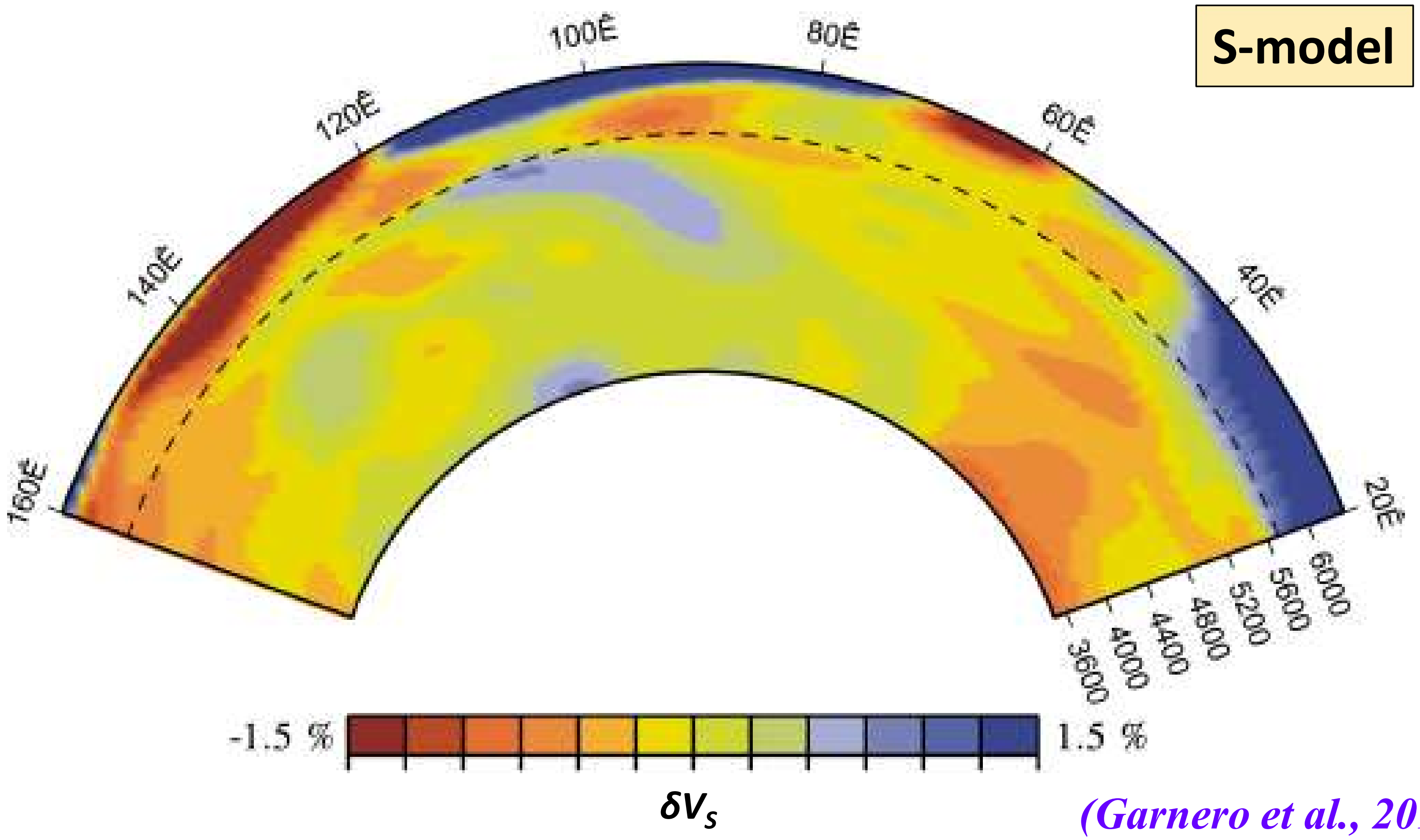
(Preliminary Reference Earth Model)

(Dziewonski & Anderson, 1981)



(Density from free oscillations)

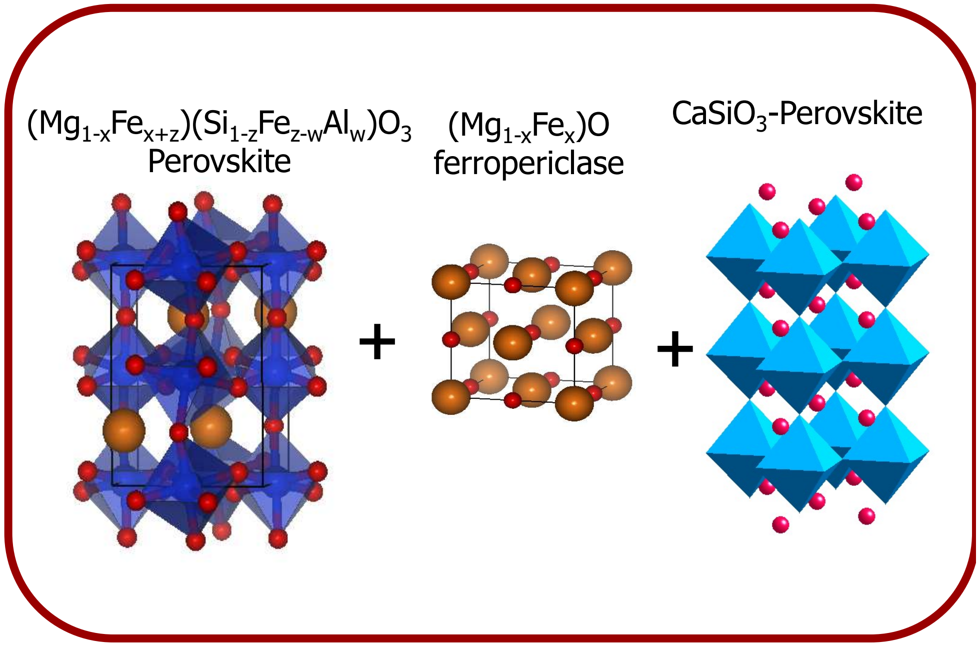
Making sense of mantle heterogeneities (Seismic Tomography)

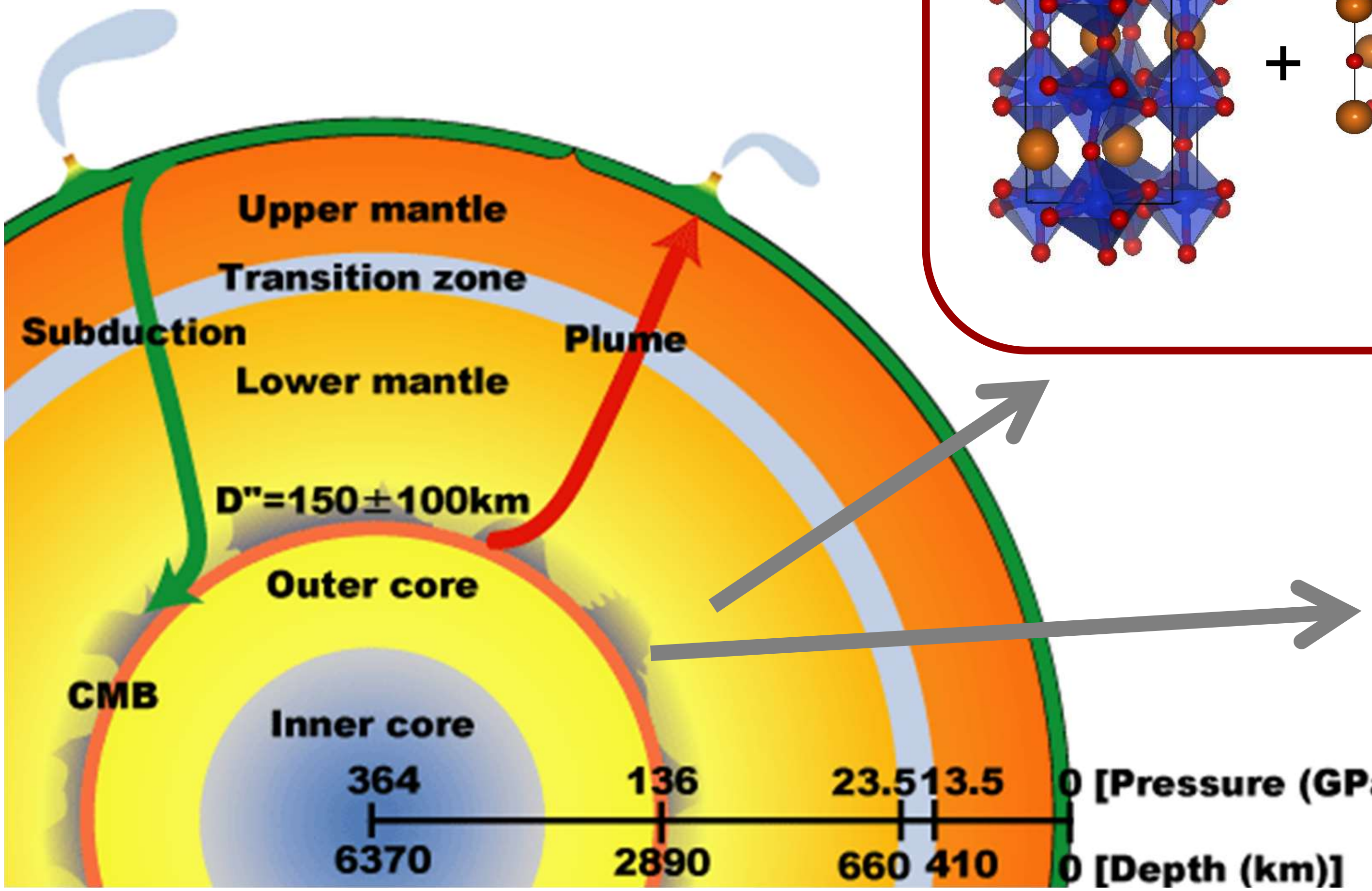


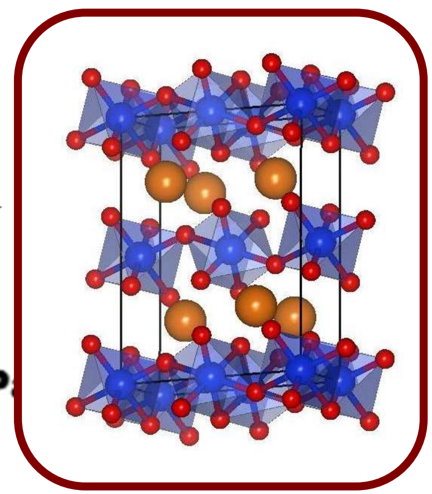
(Garnero et al., 2011)

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







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 spin crossover in the mantle (1D and 3D models)
- Acknowledgments

Acknowledgments

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- Koichiro Umemoto (ELSI, Tokyo)
- Taku and Jun Tsuchiya (Ehime, Japan)
- Fawei Zhang
- Dave Yuen (U. of Minnesota, Columbia U.)
- Maxim Ballmer (ETH-UCL)
- John Hernlund and Christine Houser (ELSI, Tokyo)
- Grace Shepard (U. of Oslo)
- Matteo Cococcioni (EPFL, Lausanne)
- Stefano de Gironcoli (SISSA, Trieste)
- Peter Blaha (Vienna, Austria)

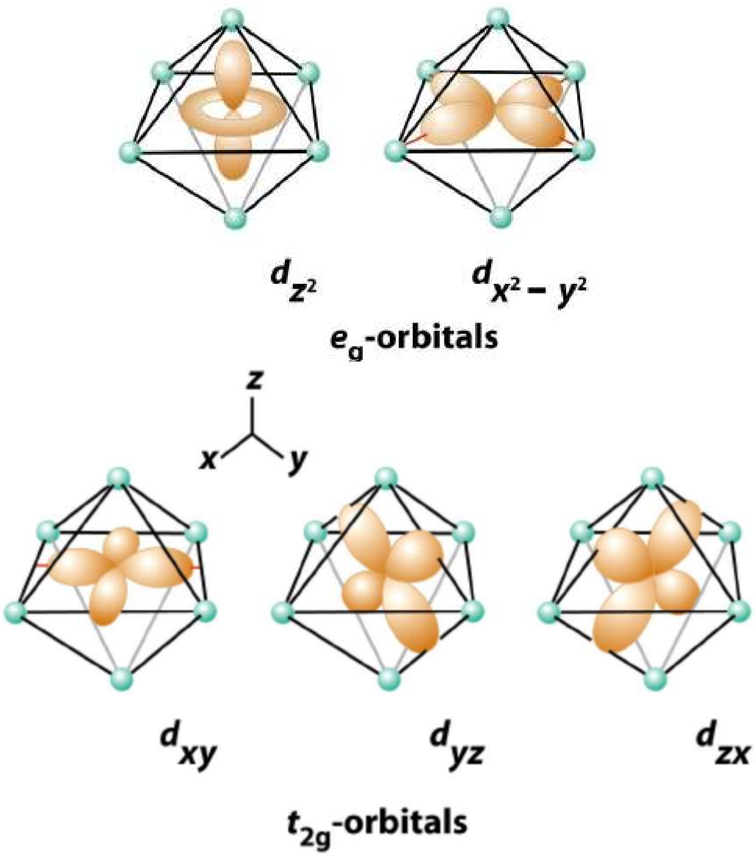
Methods

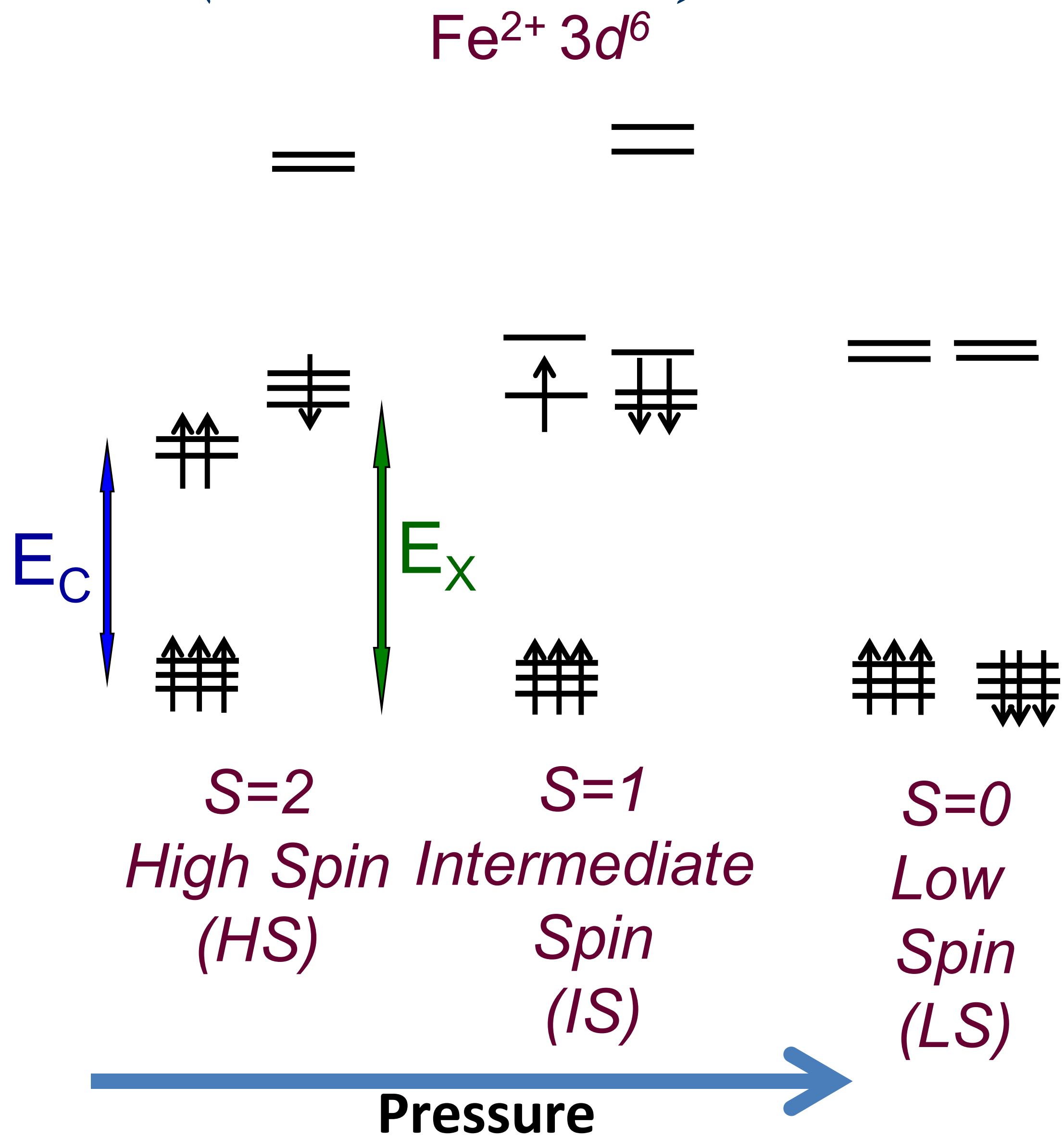
- ***Ab initio variable cell shape molecular dynamics***
  *(Wentzcovitch and Martins, 1993)**
- ***Self-consistent DFT+U***
  (Cococcioni and de Gironcoli, 2005)
- ***Density Functional Perturbation Theory + U for phonons***
  (Floris, de Gironcoli, Gross, Cococcioni, 2011)
- ***Quantum ESPRESSO and 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)

d-electrons in crystal field

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





Spin transition (or crossover)

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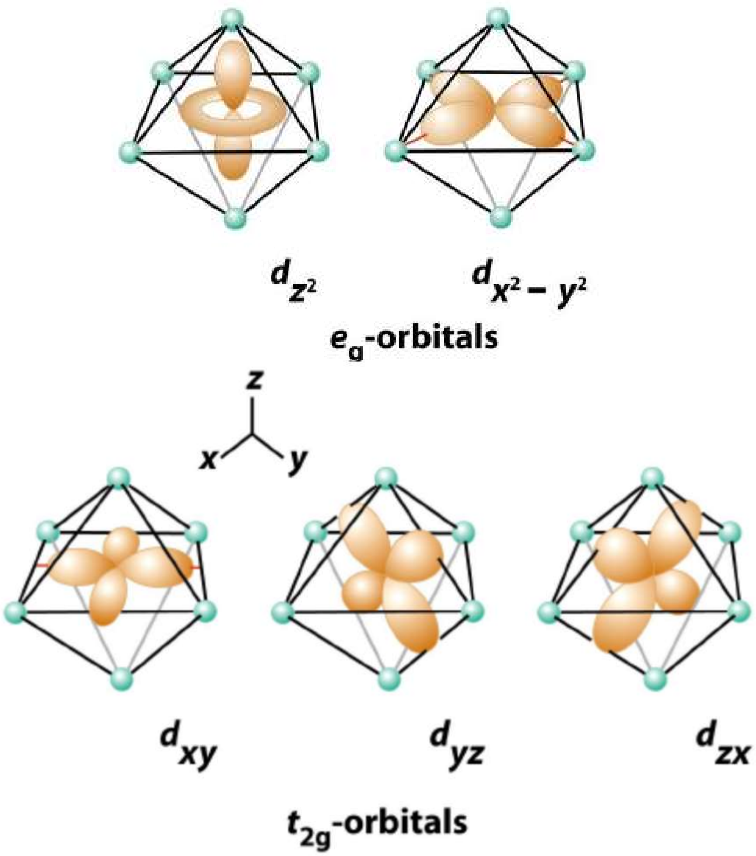
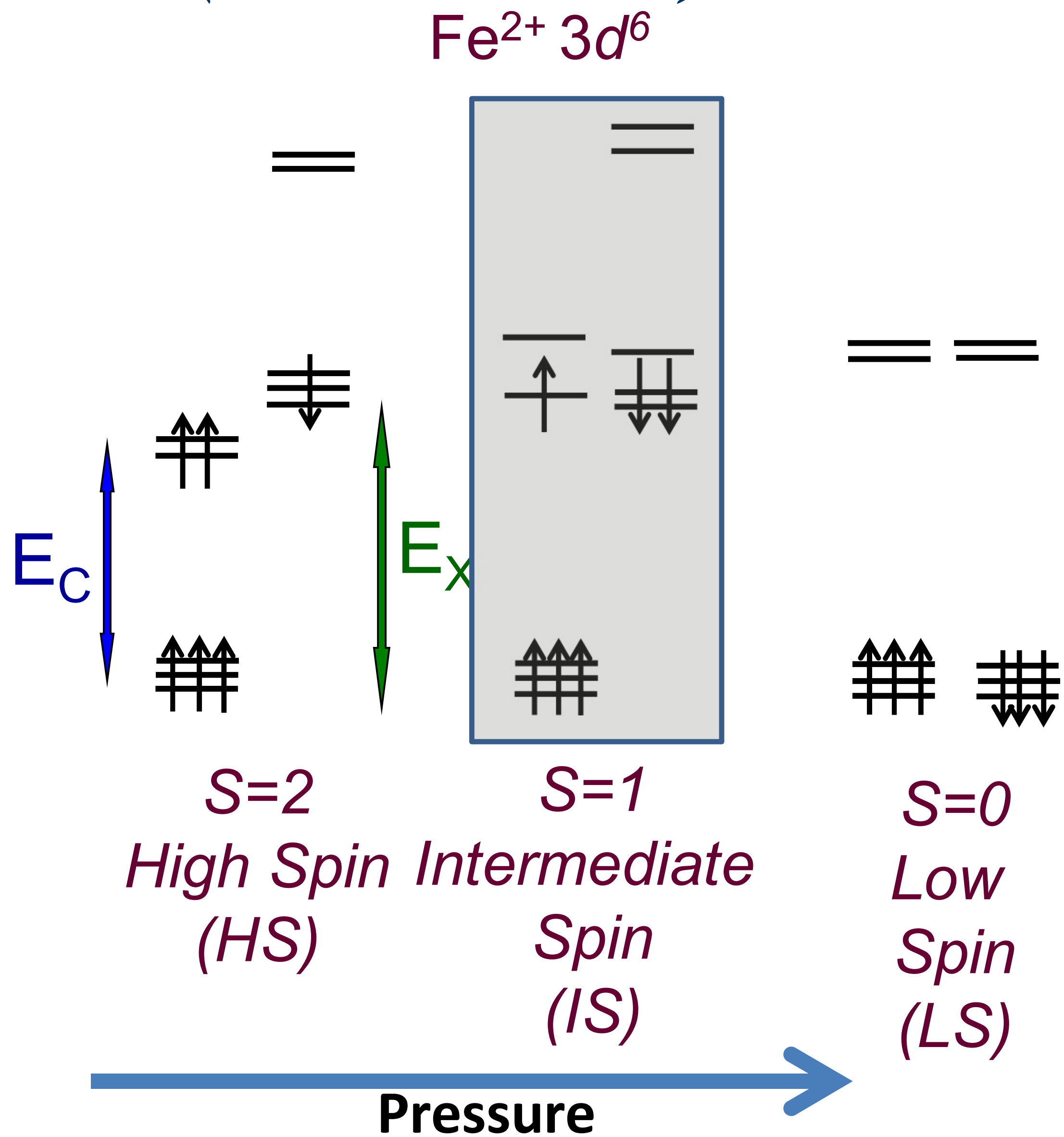
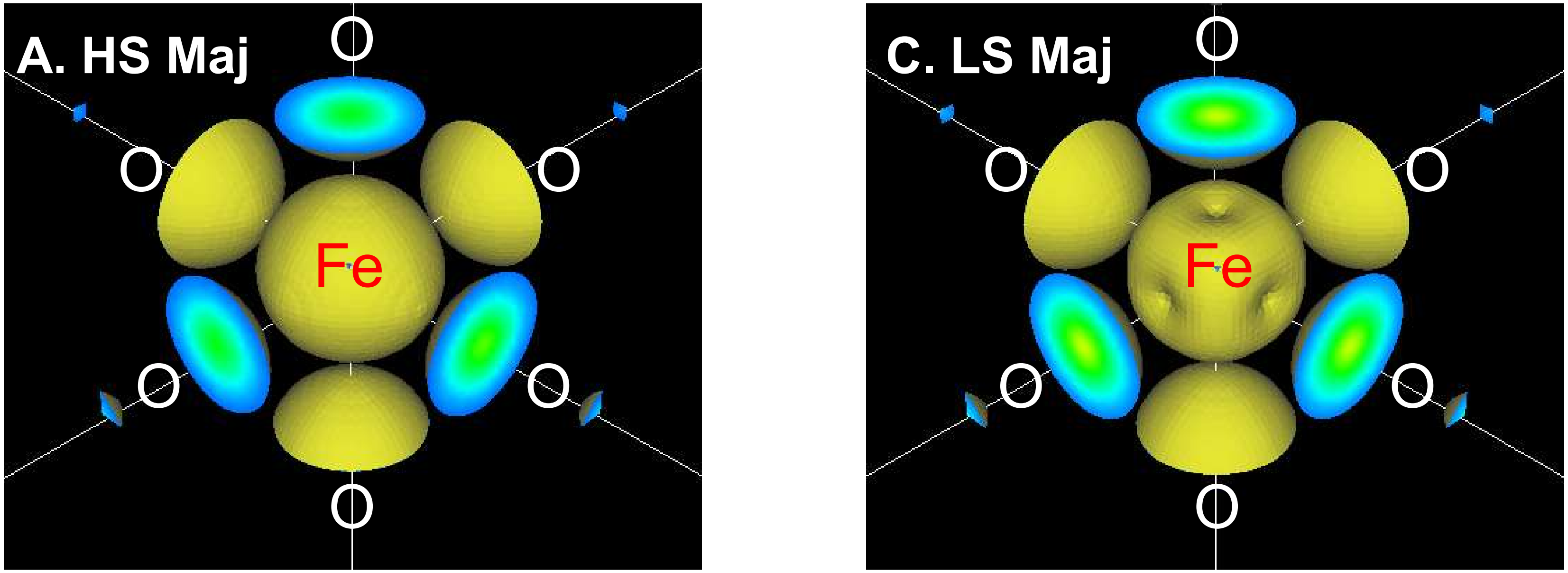
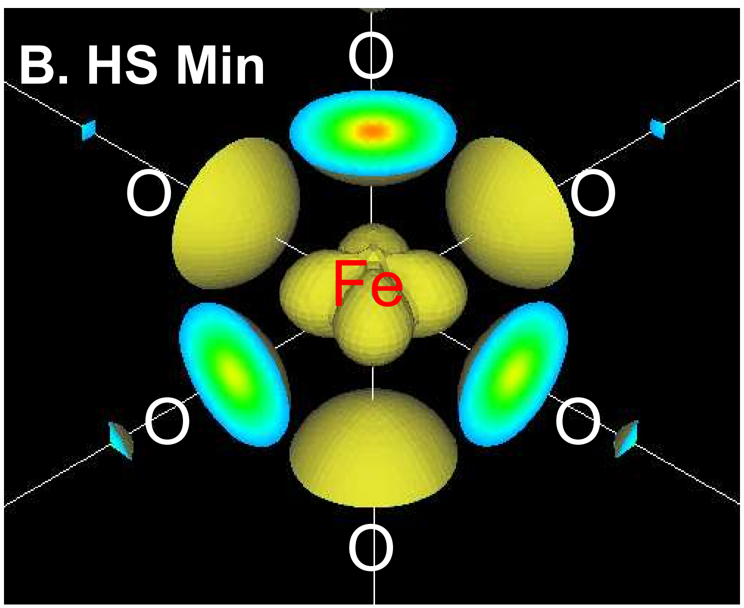




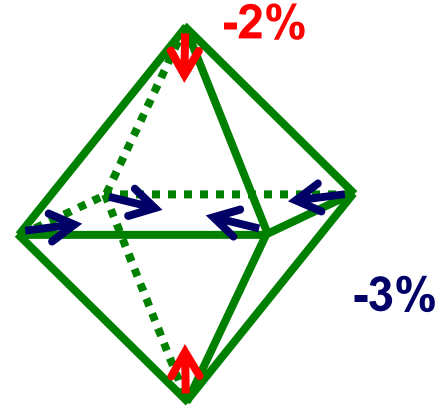
Ferropericlase

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



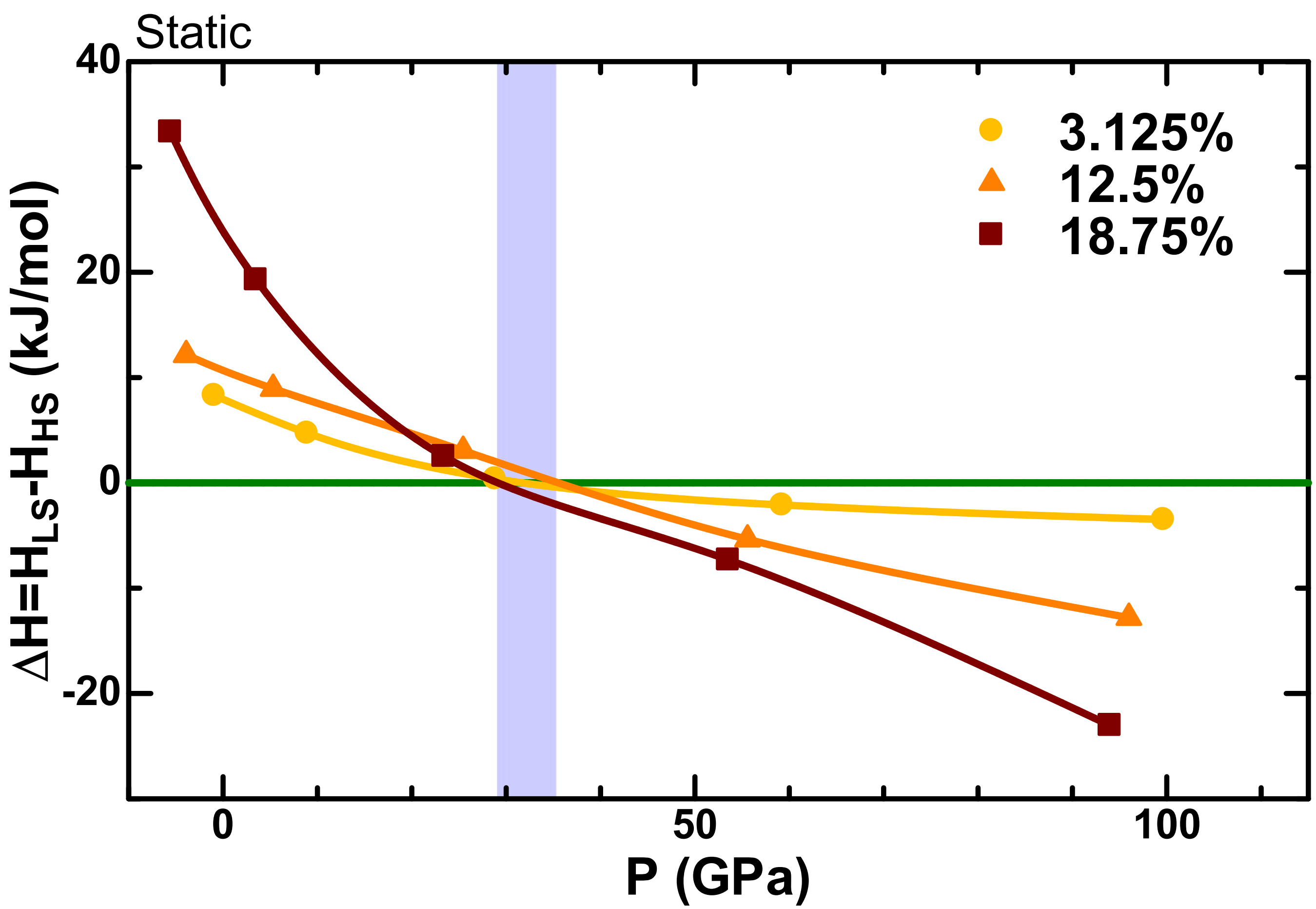


ΔV_{oct}~-8%



Tsuchiya, PRL (2006)

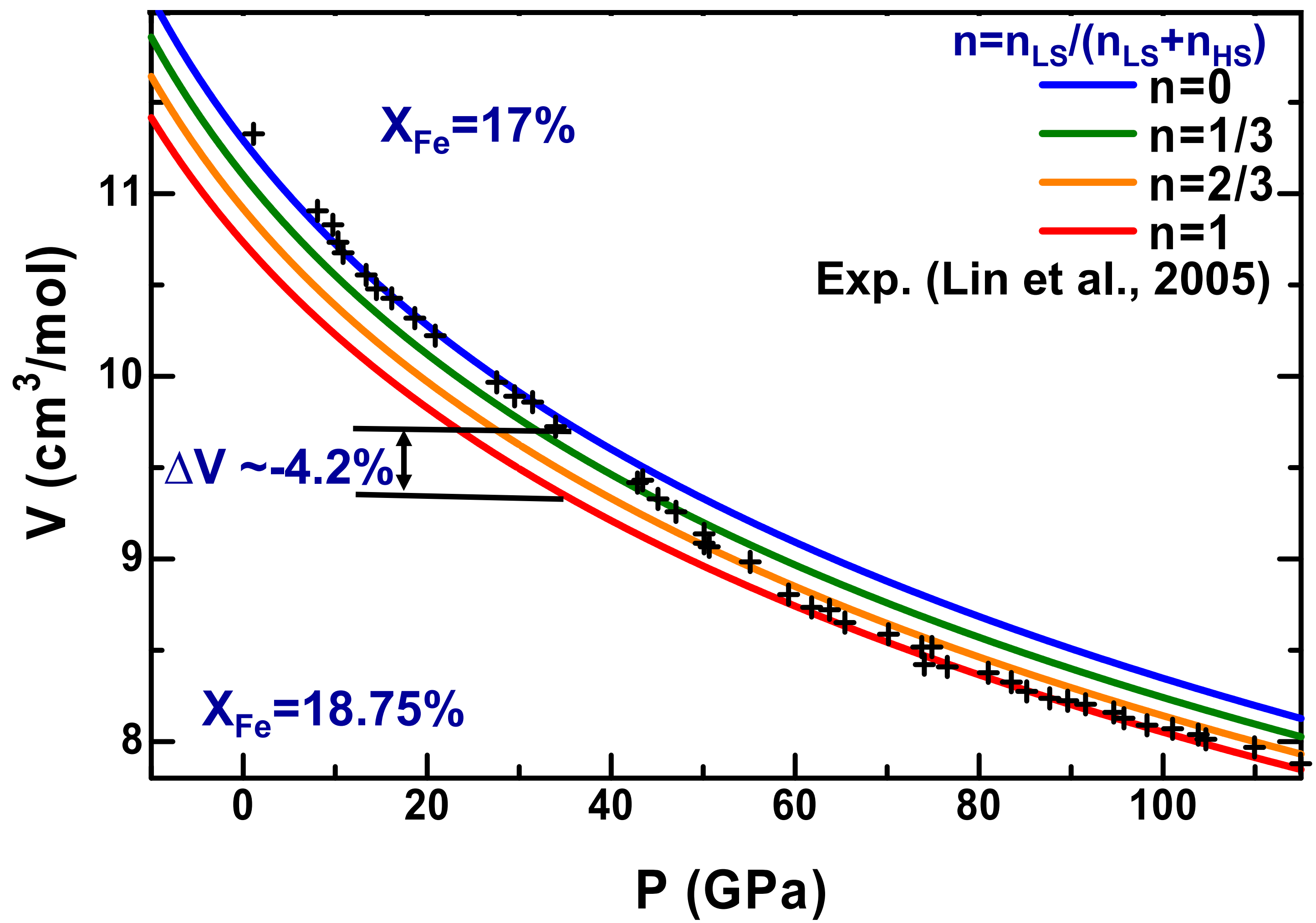
HS-to-LS "transition"



$P_T = 32 \pm 3$ GPa

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

Static equation of state



Tsuchiya et al., PRL (2006) $\Delta V_{HS\text{-}LS} = -2.22\ nX_{Fe}\ cm^3/mol$

Thermodynamics

Quasi-ideal solid solution of HS and LS ferropericlase
(x_{Fe} = cte)

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

Quasi-ideal solid solution of HS and LS ferropericlase (x_{Fe} = cte)

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

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

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

Quasi-ideal solid solution of HS and LS ferropericlase
(x_{Fe} = cte)

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

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

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

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

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

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

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

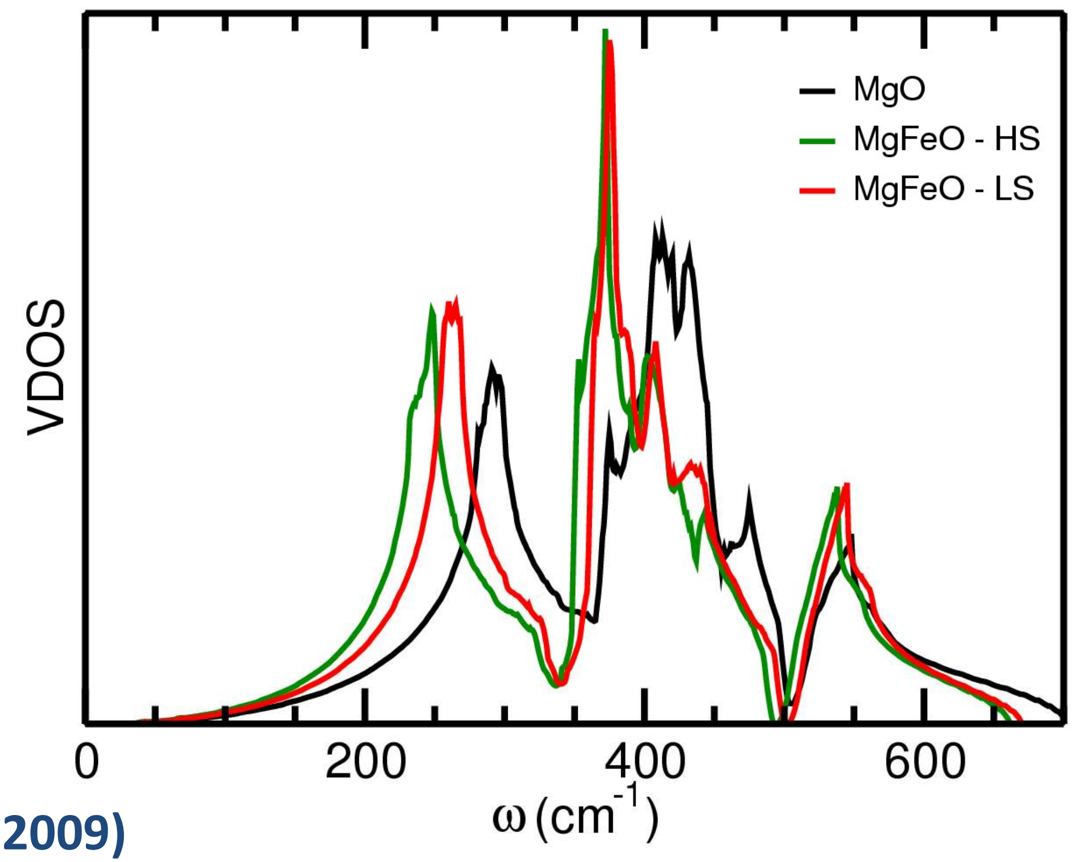
Free energy minimization

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

Vibrational Virtual Crystal Model

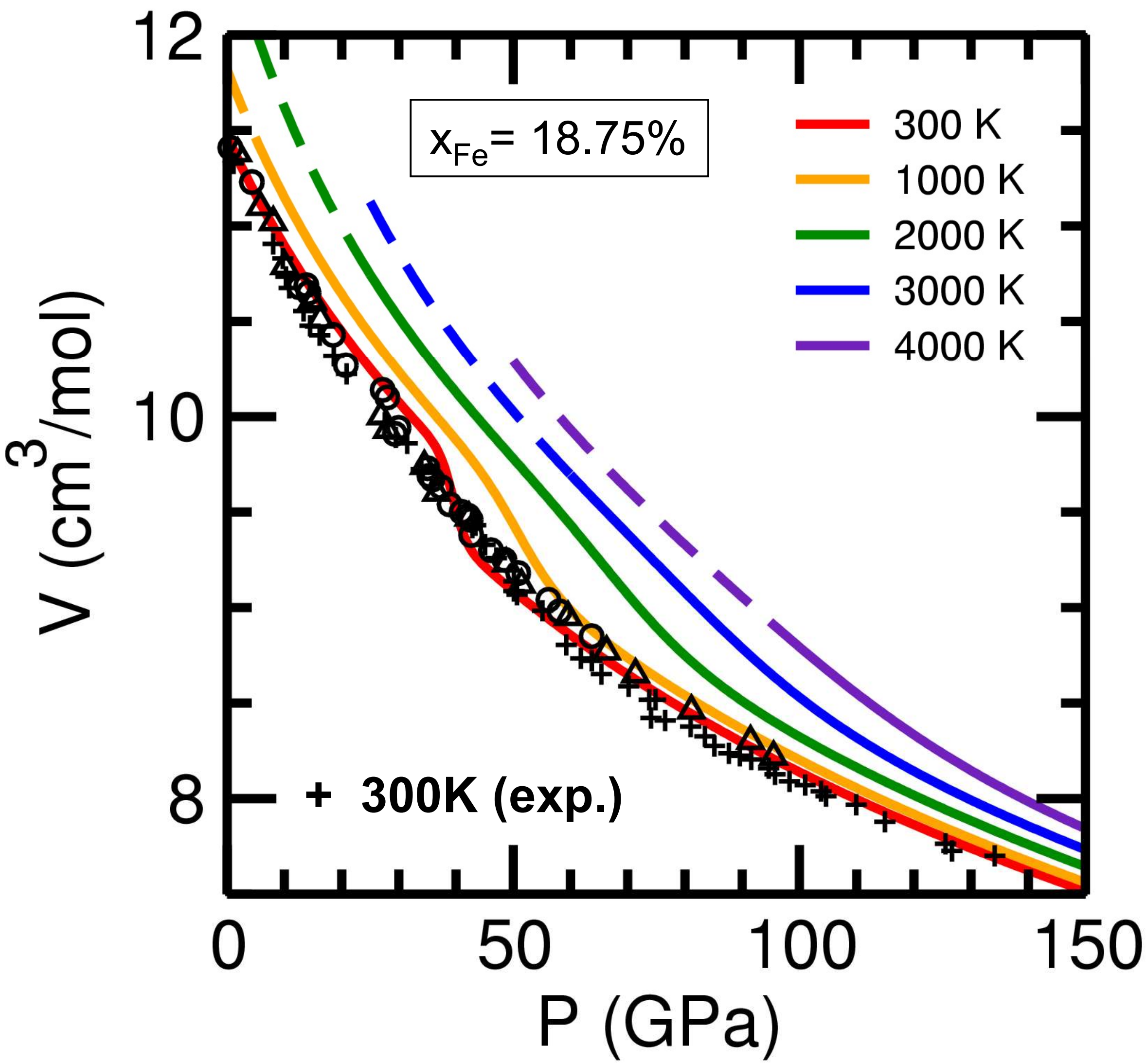
- Replace Mg mass by the average cation mass of the alloy

- Replace “some” inter-atomic force constants of MgO to reproduce the that the static elastic constants of the alloy



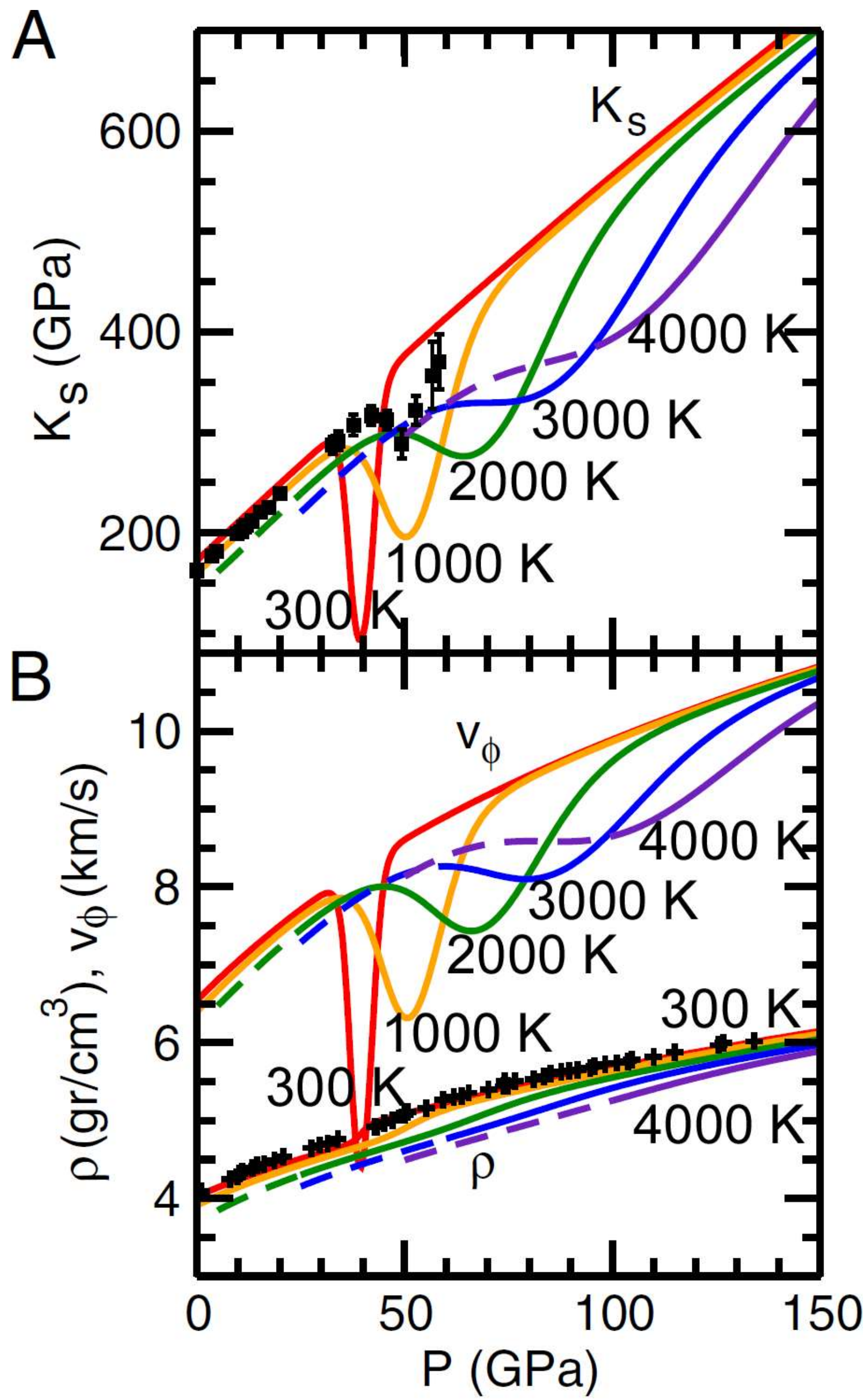
Wu et al, PRB (2009)

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



+ 300K (exp.)

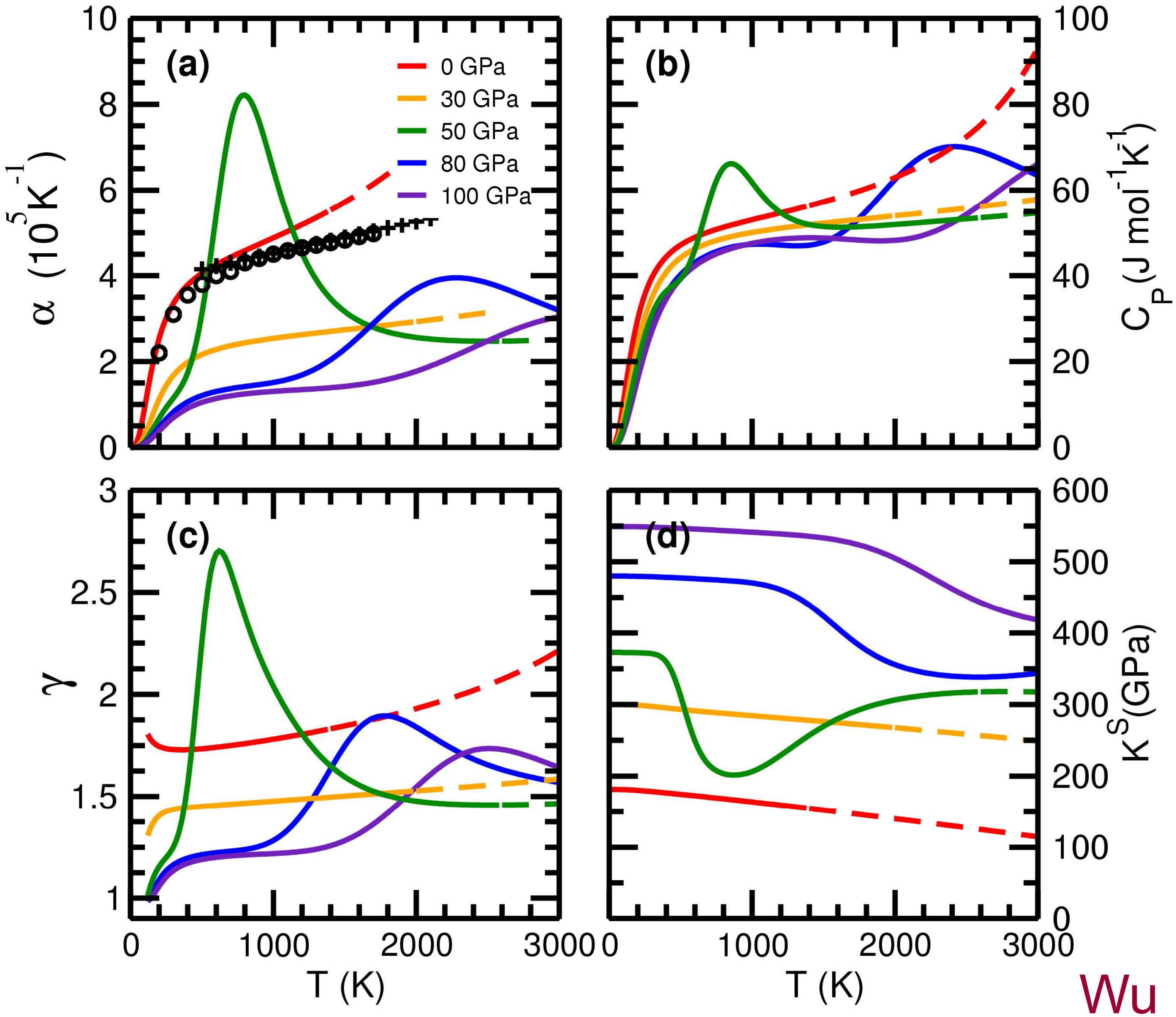
+ Experiments (Lin *et al*., *Nature,* 2005) (x_{Fe}=17%, RT)
o and Δ (Fei *et al*., GRL*,* 2007) (X_{Fe}=20%, RT)



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

Exp: Crowhurst et al, Science 2006

Thermodynamics properties x_{Fe}= 18.75%



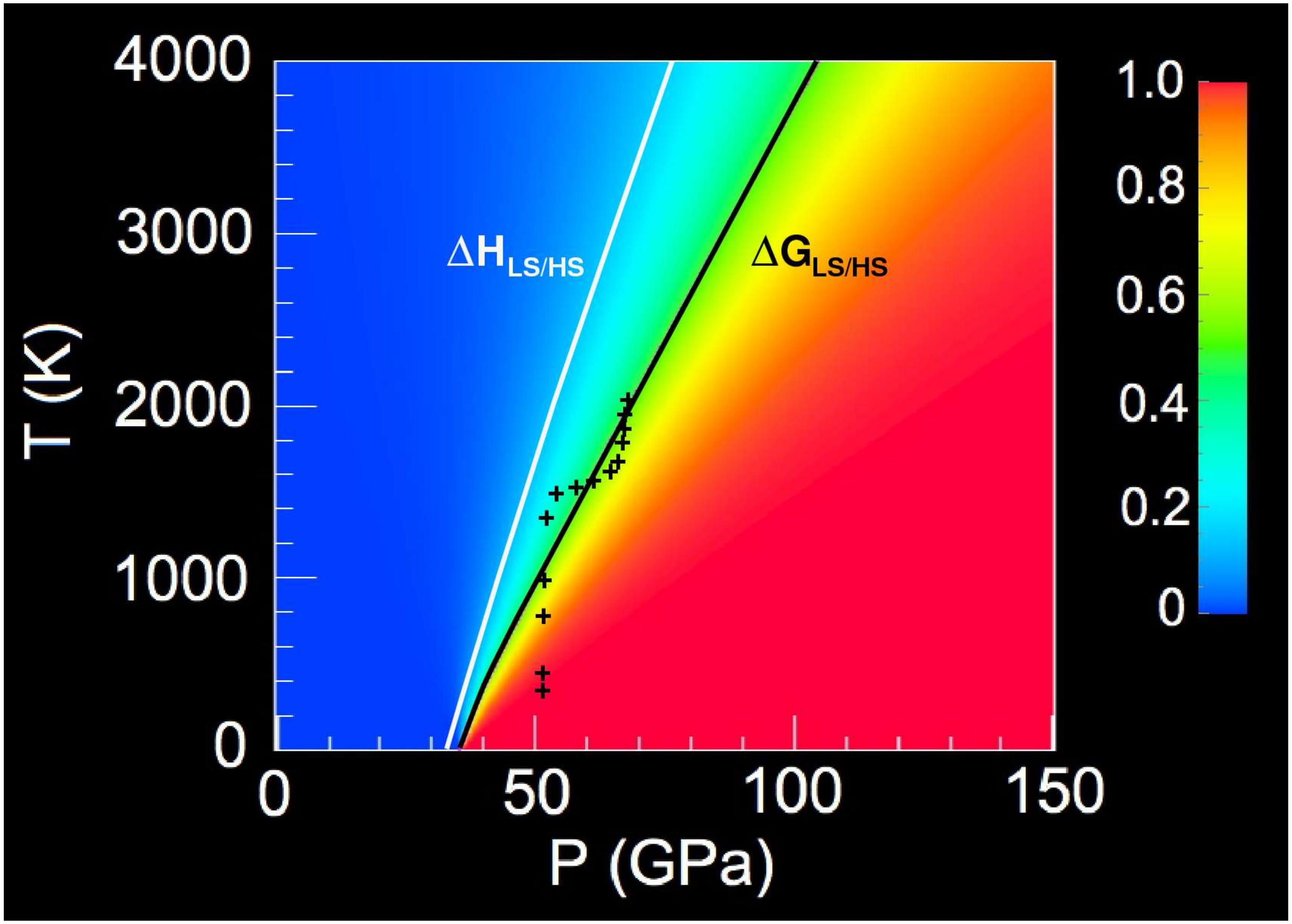
Experiments
(o x_{Fe}=0 and += 40%)

300K (exp.)

Wu et al, PRB 2009

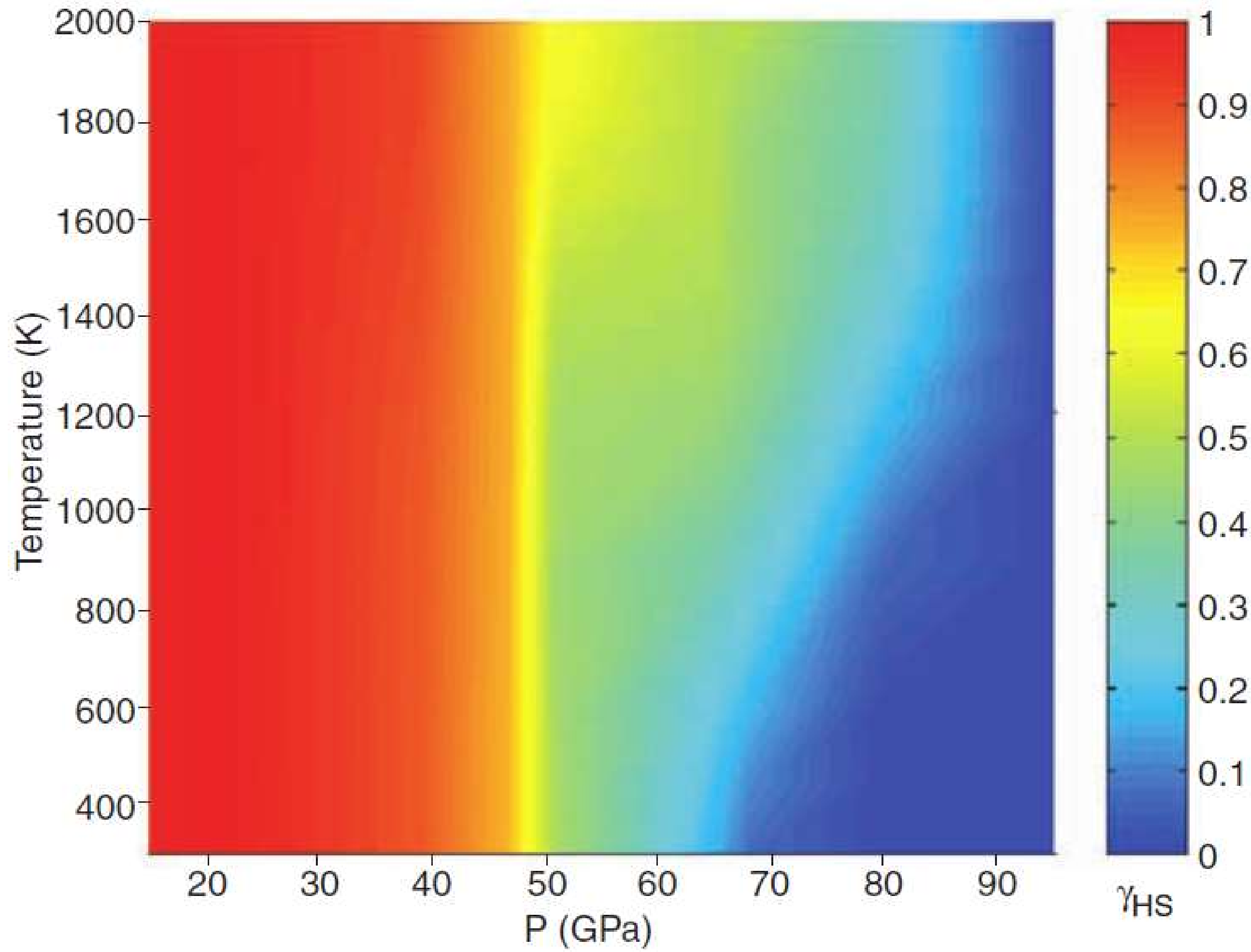
LS fraction n(P,T)

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



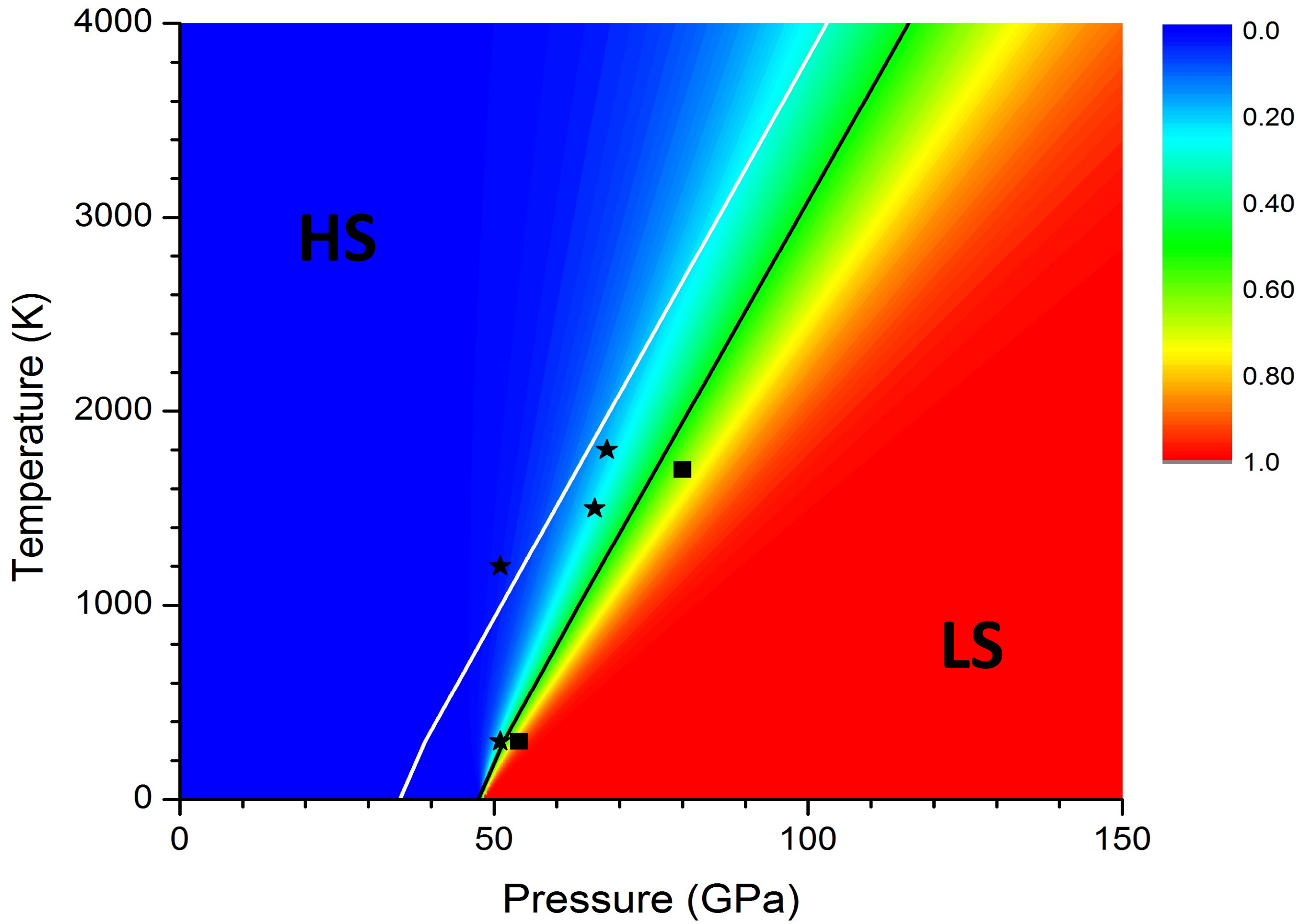
x = 0.17 Lin *et al., Science* (2007)

LS fraction n(P,T)



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

Free energy shift ($E_{HS} – E_{LS}$ = - 0.06 eV/Fe):



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

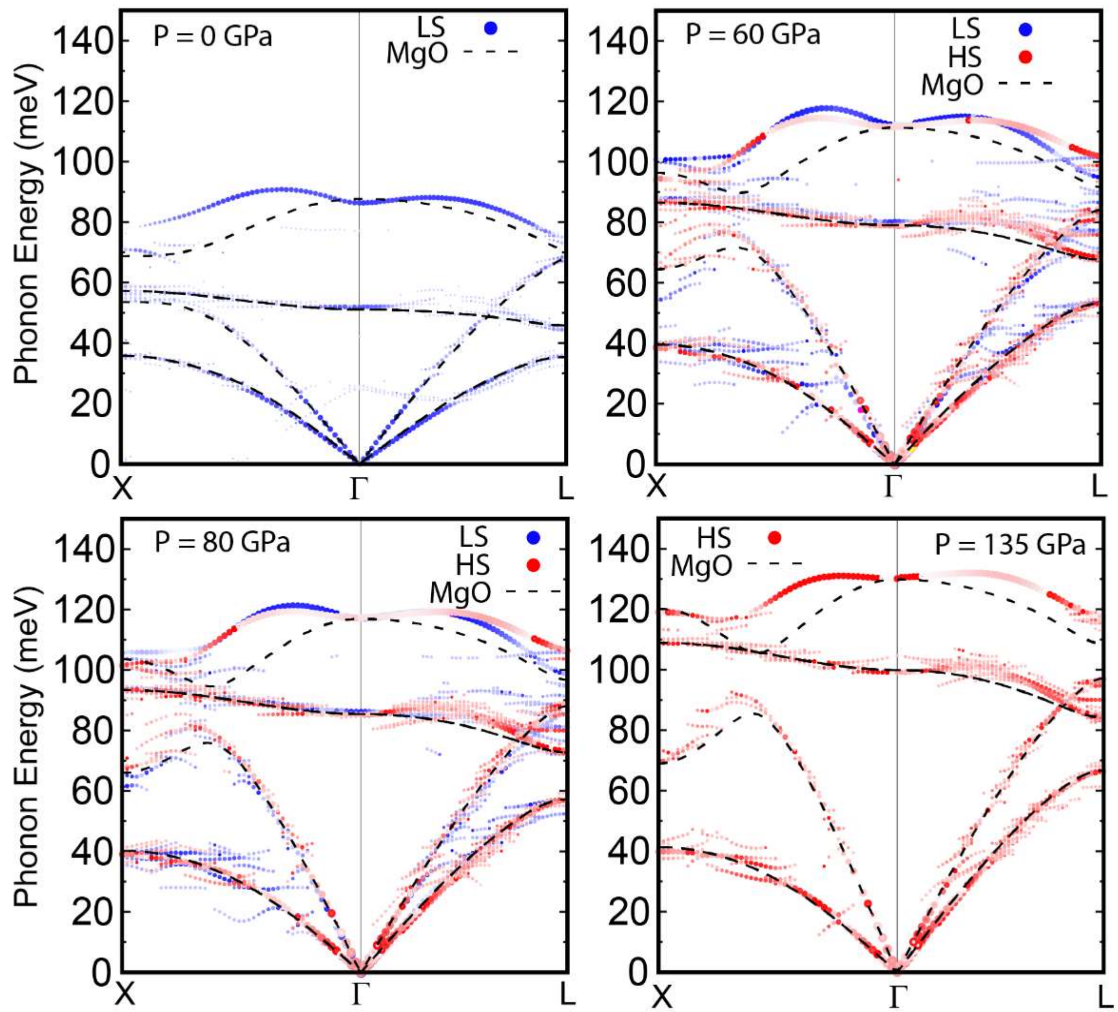
★ *Lin et al., Science* (2007) x=0.17

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)*

Vibrational properties across the spin crossover

- No unstable phonons throughout the spin crossover in Fp



x_{Fe} = 3.125%

Marcondes, Zhang, & Wentzcovitch, PRB under review (2020)

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)

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

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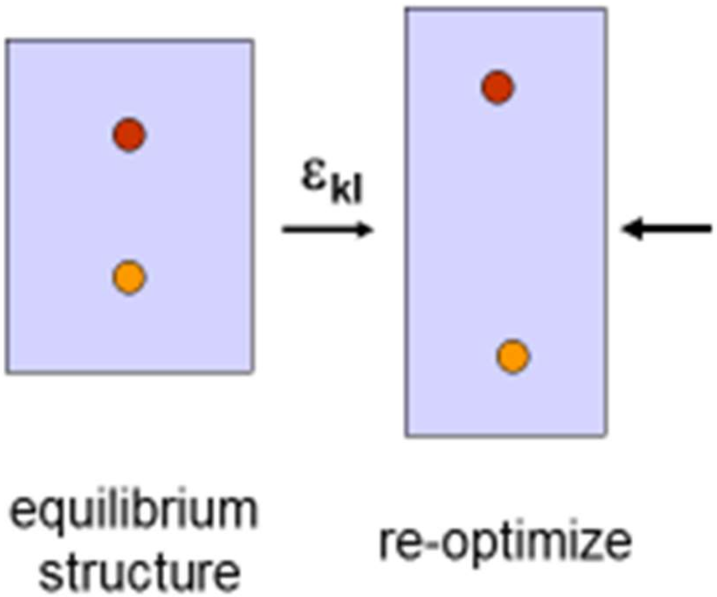
- **Compliances:**

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

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

High Temperature Elastic Tensor

Karki et al., Science (1999), Wentzcovitch et al., PRL (2004), Wu & Wentzcovitch, PRB (2011)

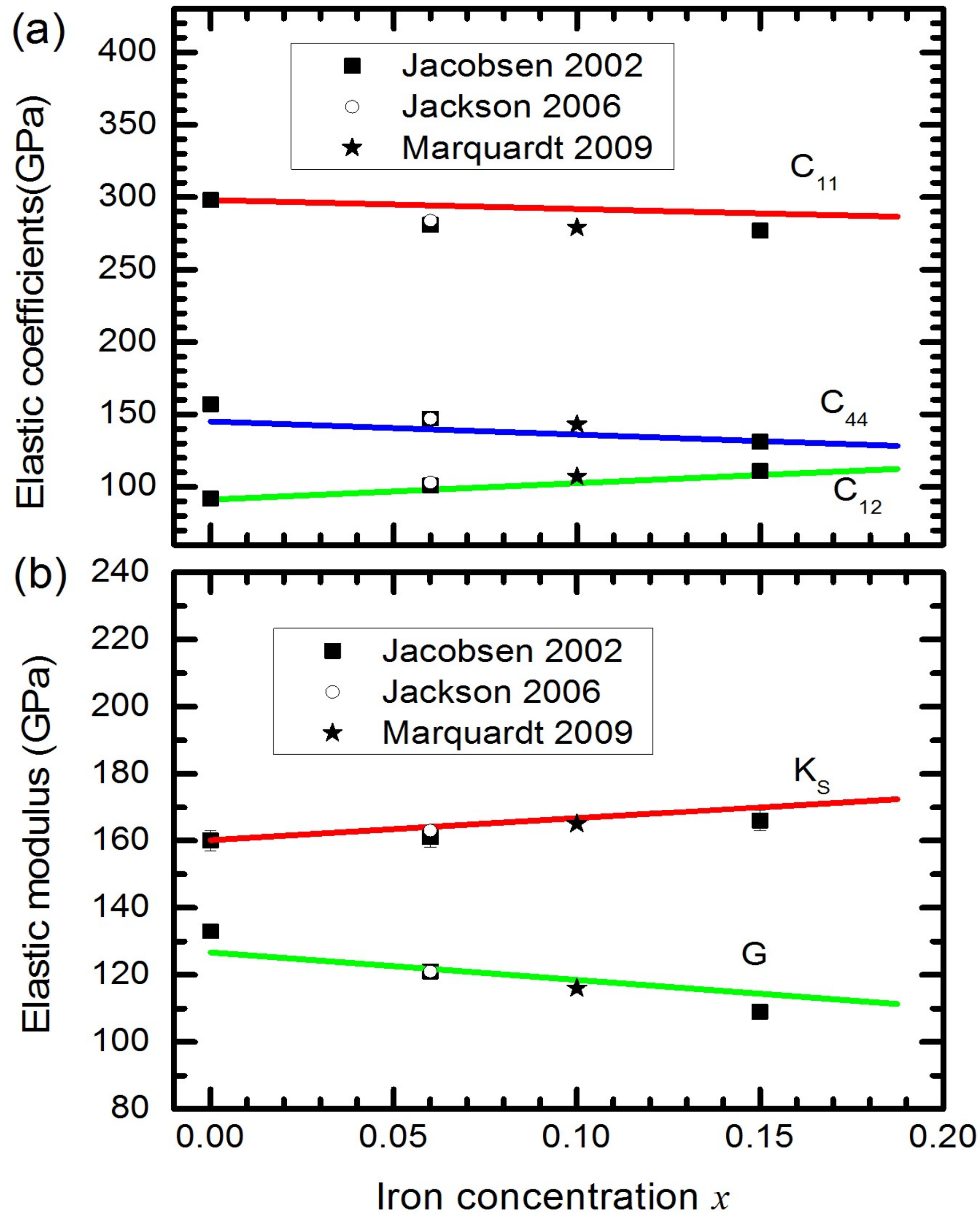


$$c_{ij}^{T}(T,P) = \left[\frac{\partial^2 G}{\partial \varepsilon_i \partial \varepsilon_j}\right]_P$$

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

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

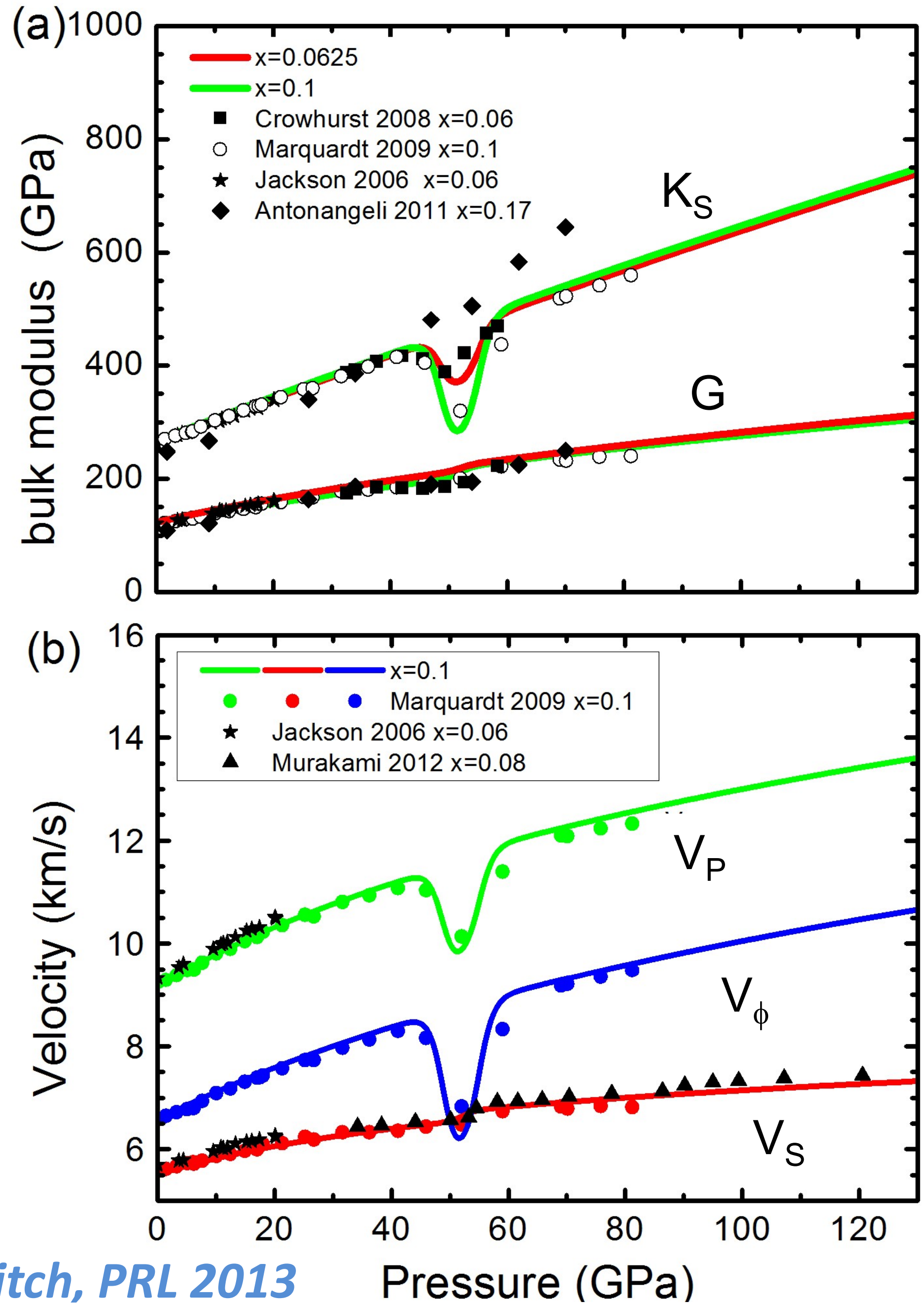
T = 300 K
P = 0 GPa



(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



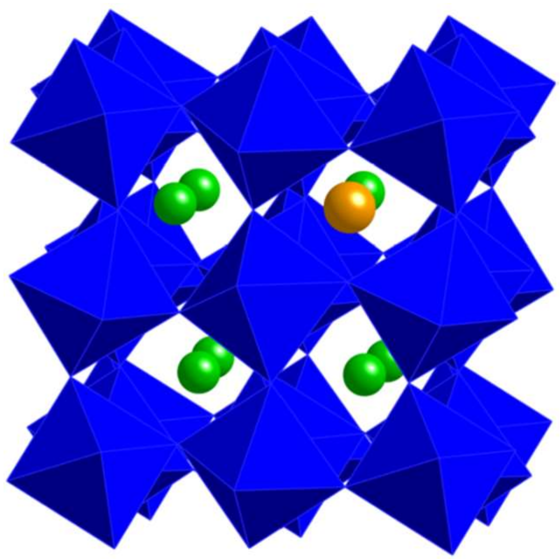
$$V_P = \sqrt{\frac{K_S + \frac{3}{4}G}{\rho}}$$

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

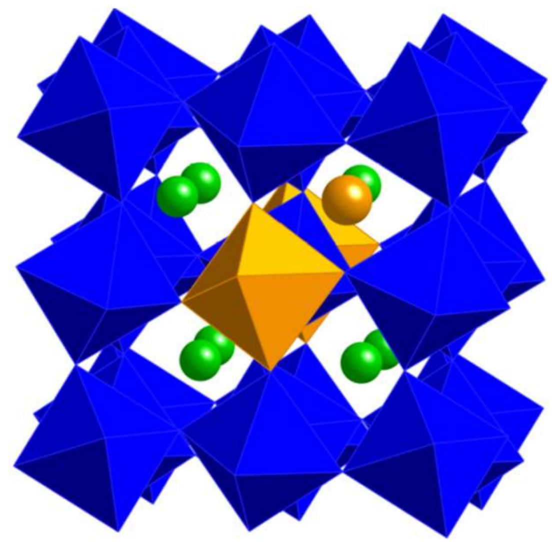
$$V_S = \sqrt{\frac{G}{\rho}}$$

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

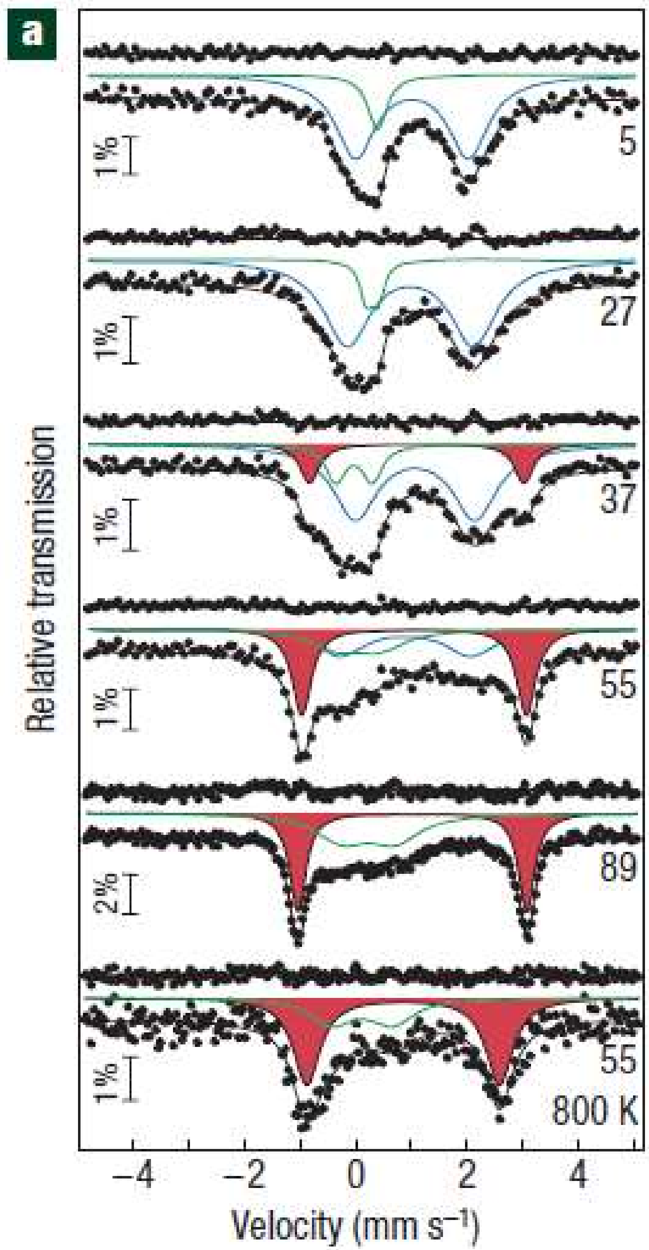
- “New” Fe^{2+} (QS = 3.5 mm/s) for *P* > 30 GPa

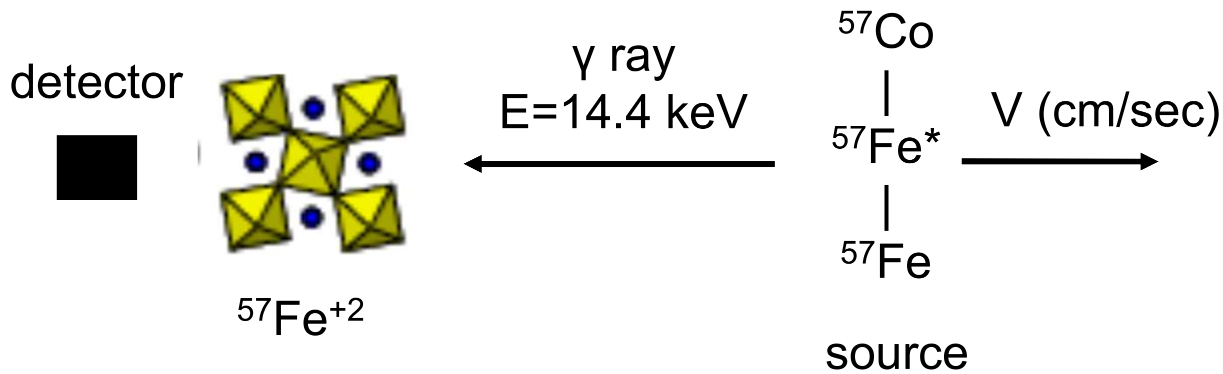
- Fe^{2+} QS = 3.5 mm/s increases at the expense of the HS Fe^{2+} (QS = 2.4 mm/s)

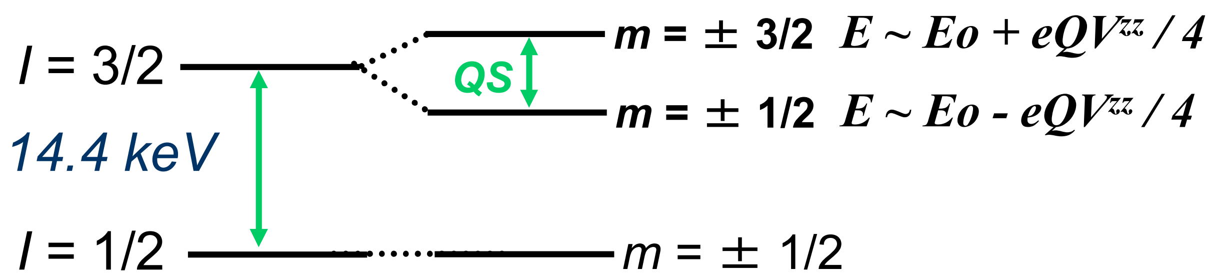
- The two sets of peaks “merge” at P ~ 60 GPa

McCammon et al. Nature Geoscience (2008)

"New" species of Fe^{2+}: IS?







$$QS \sim eQV^{zz}/2$$

$$V^{zz} = \frac{\partial^2 V}{\partial z \partial z}$$

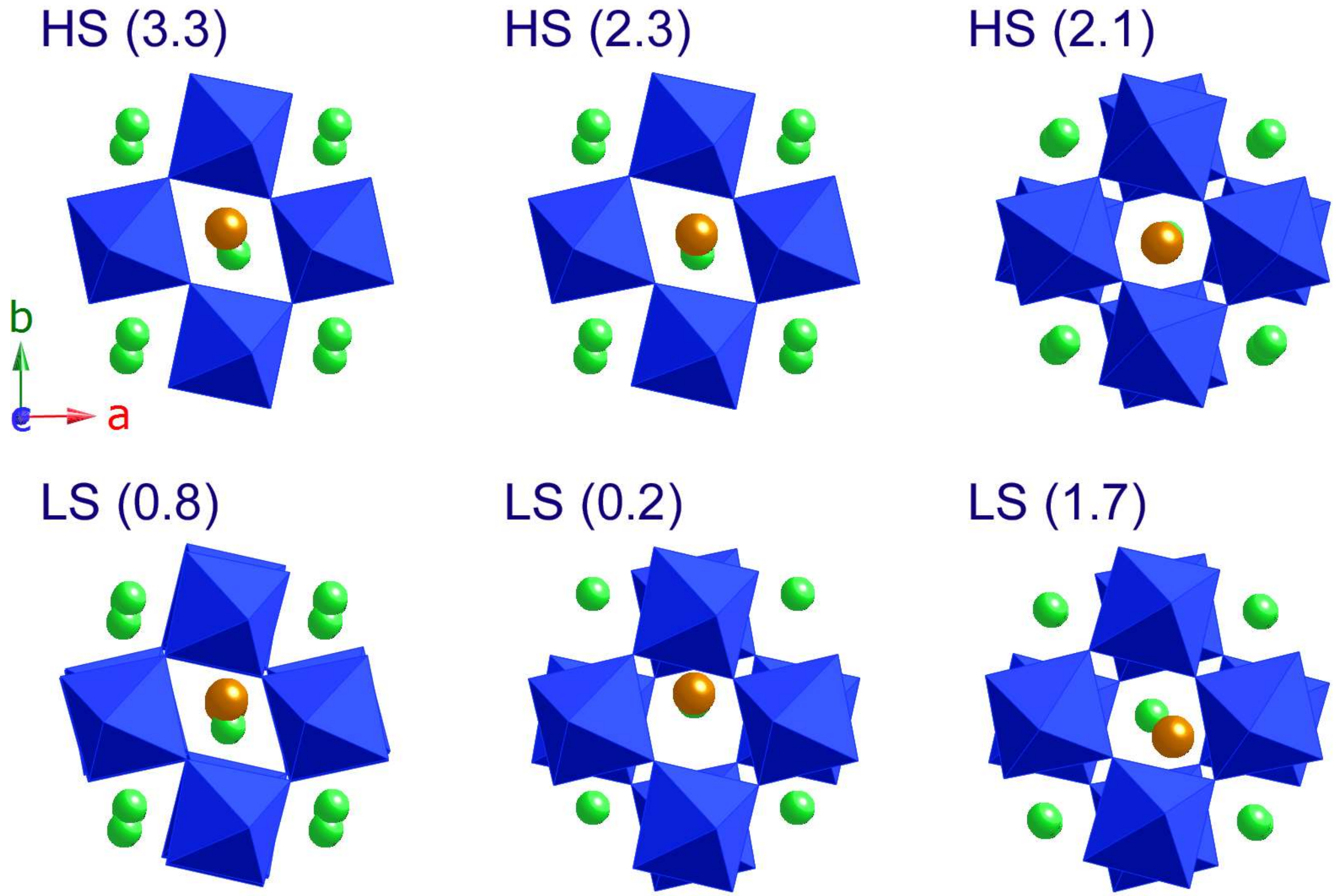
. Spin state → charge distribution → V^{zz} → QS

. Spin state cannot be derived using just QS

McCammon et al., Nature Geosciences (2008)

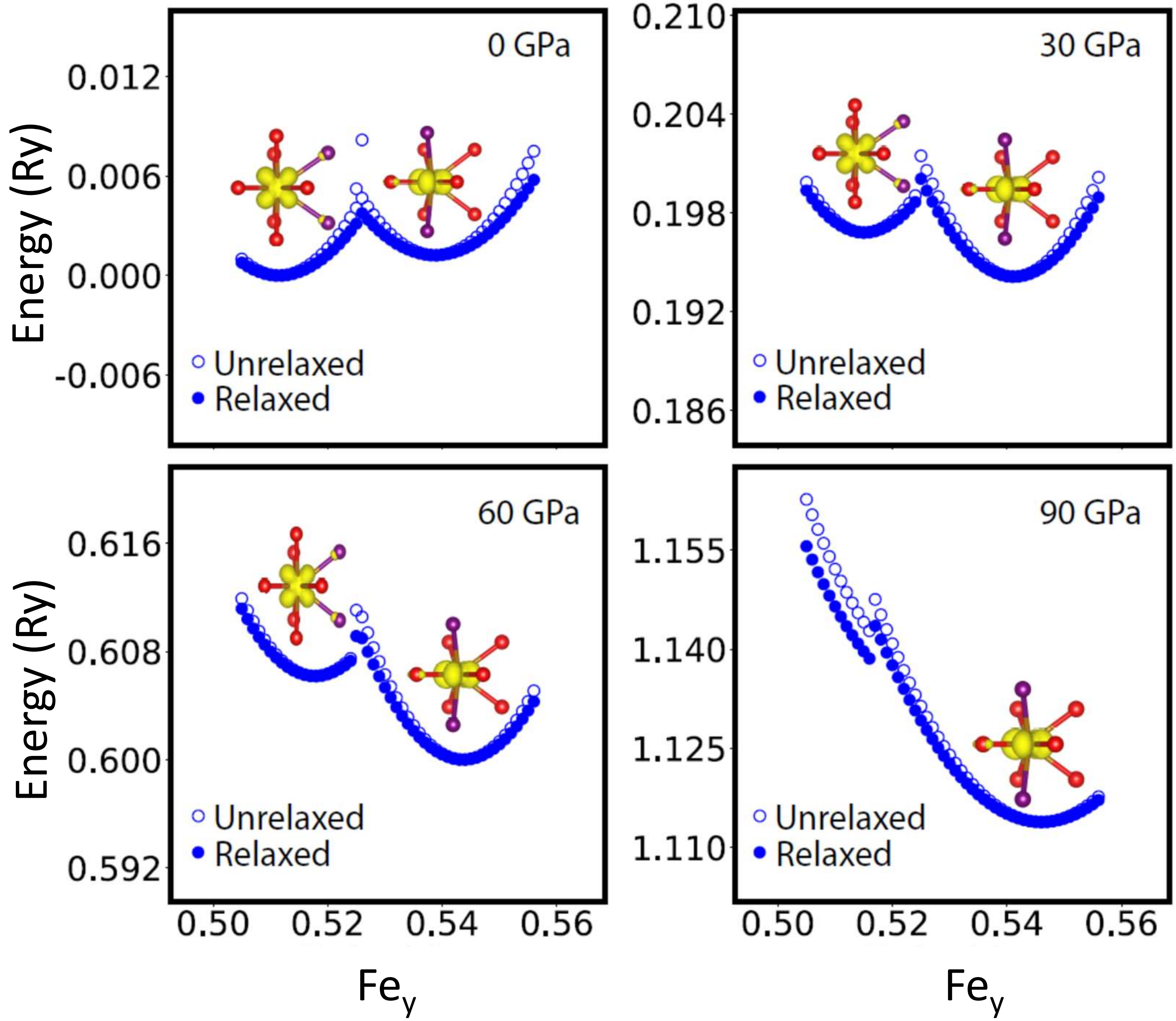
HS and LS configurations at 0 GPa

x_{Fe} = 0.25 and 0.125



Hsu, Umemoto, Blaha, and Wentzcovitch, EPSL 2009

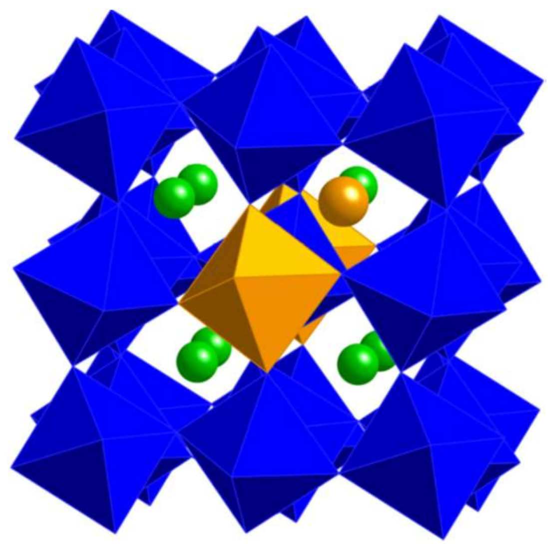
The double-well with LDA+U_{sc}



- $(Mg_{0.875}Fe_{0.125})SiO_3$
- **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)

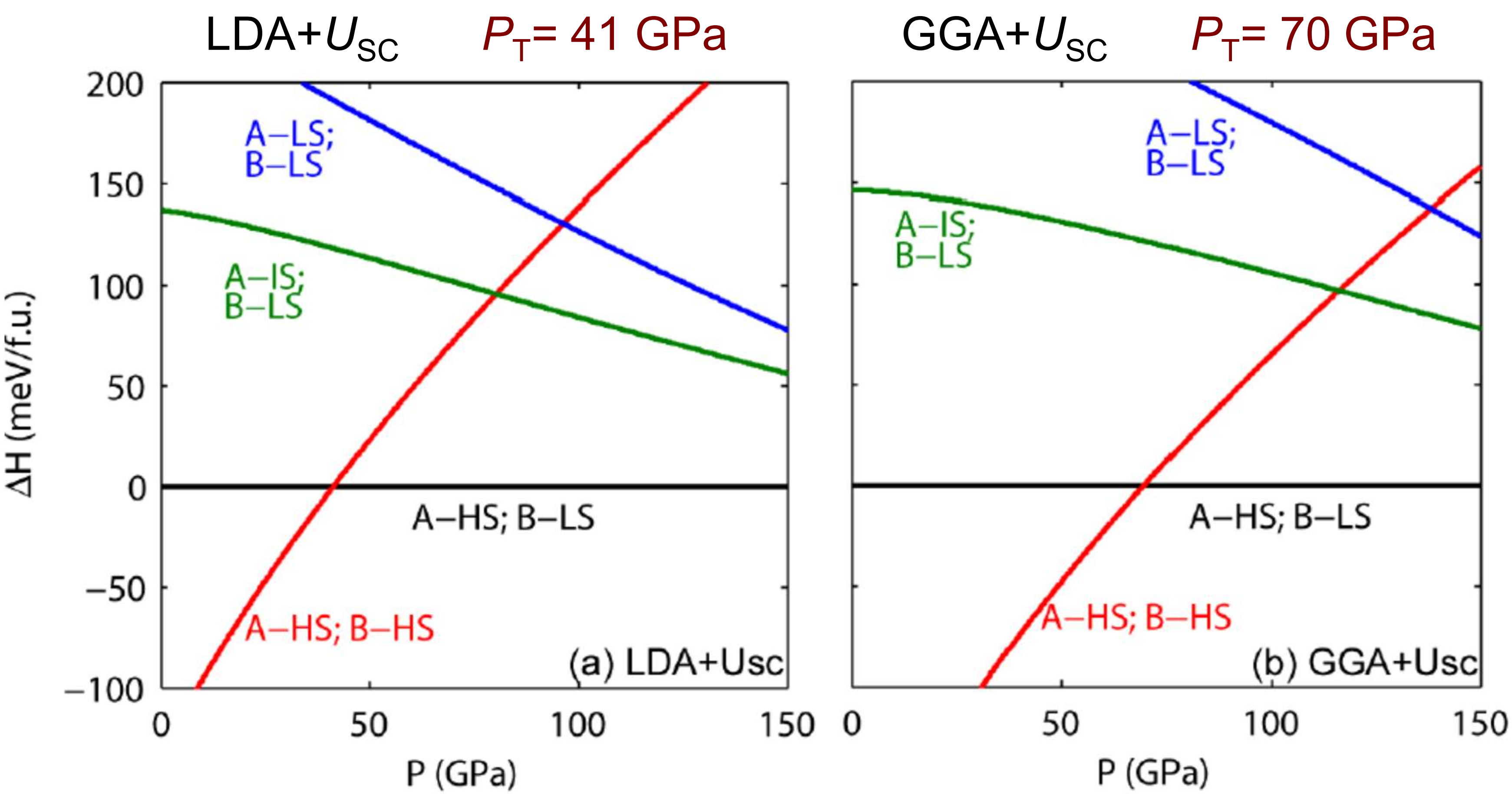
Calculations

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

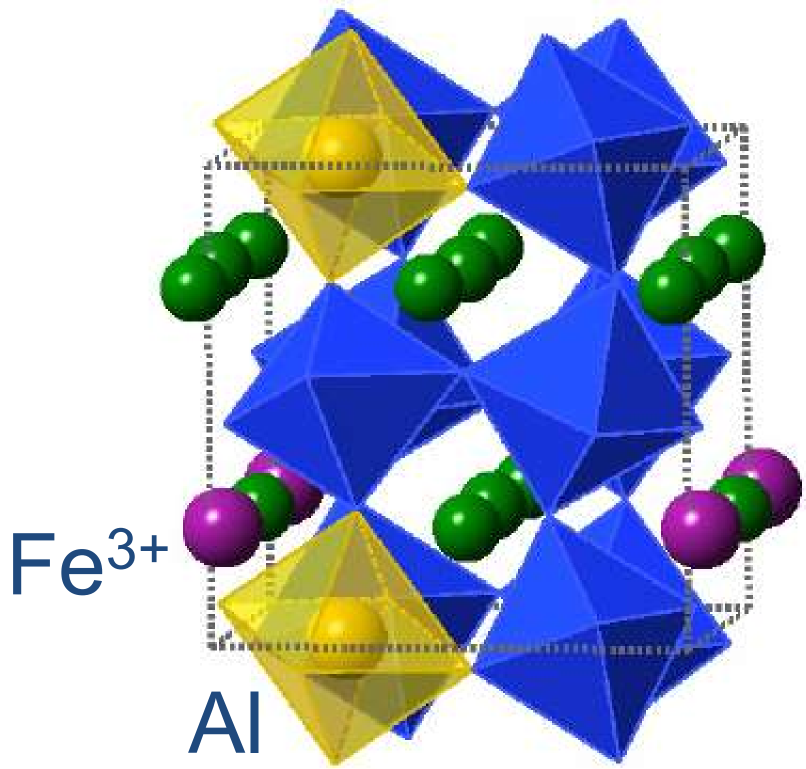
Relative Enthalpies (U_{SC})



P_T observed in XES: 50-60 GPa

Hsu *et al.*, PRL (2011)

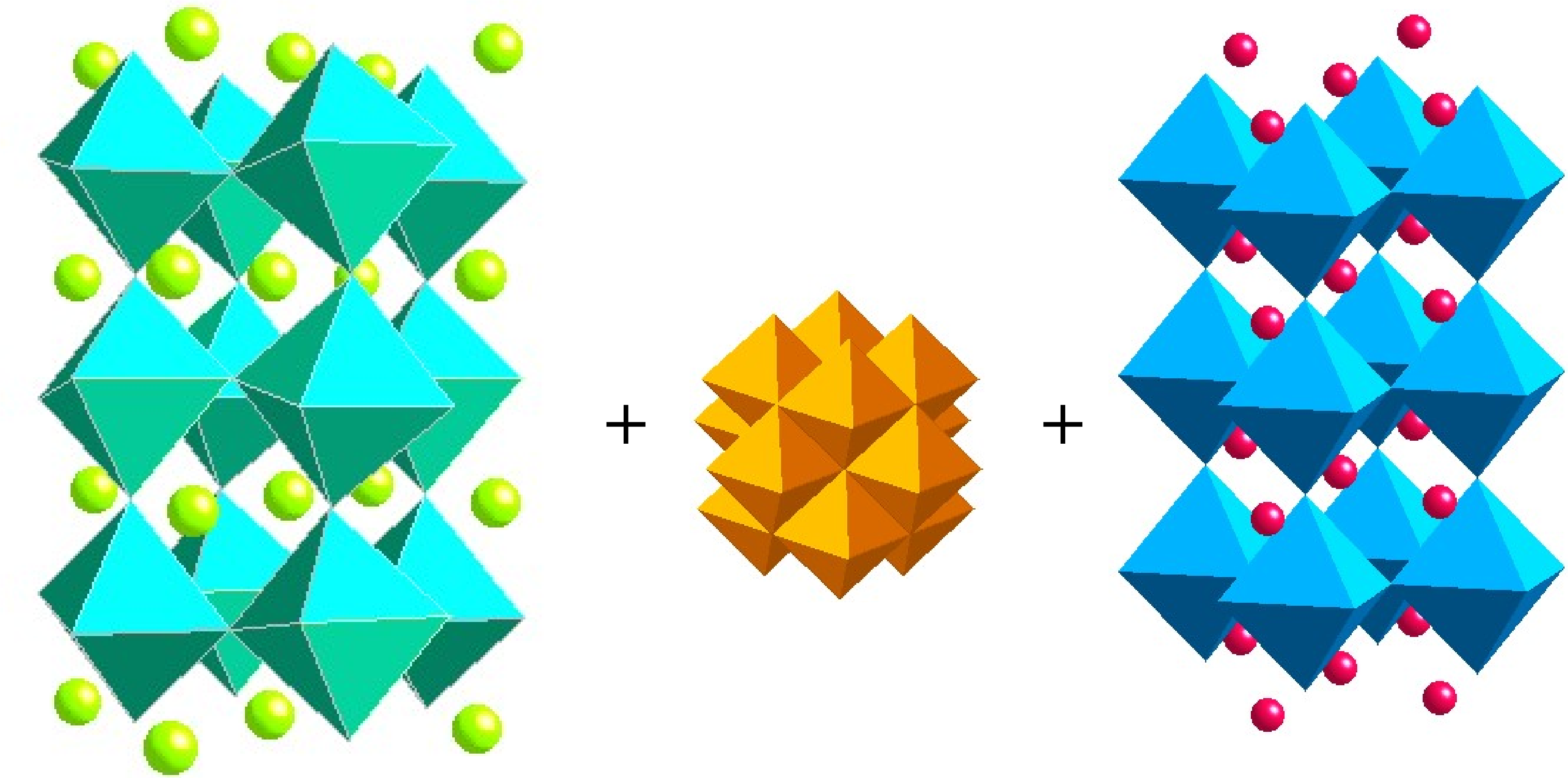
Spin crossover in aluminous Pv



Hsu, Yu, and Wentzcovitch (EPSL 2012)

Consequences for Mantle Structure

Lower Mantle



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

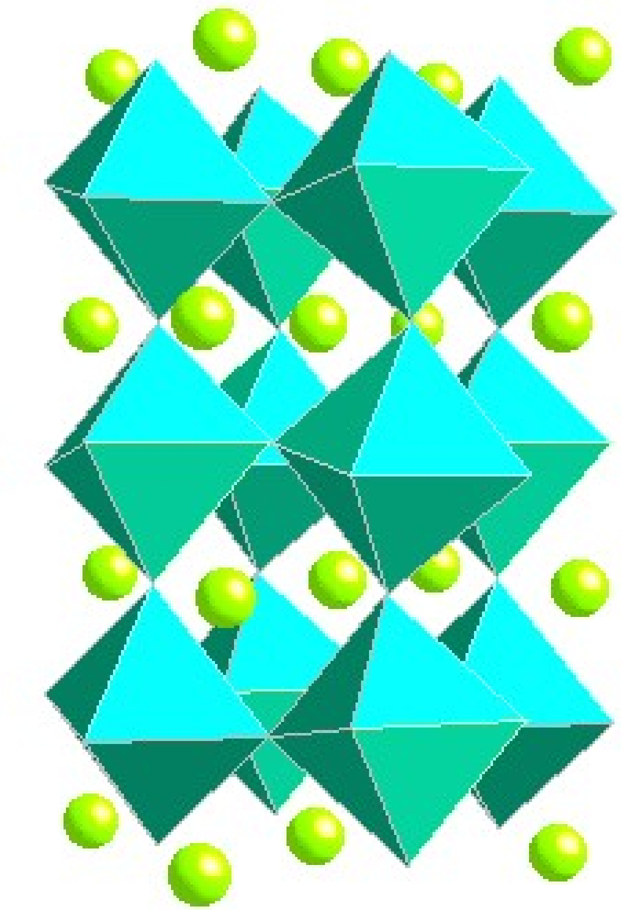
$(Mg_x,Fe_{(1-x)})O$

$CaSiO_3$

Lower Mantle

How much ferropericlase

?



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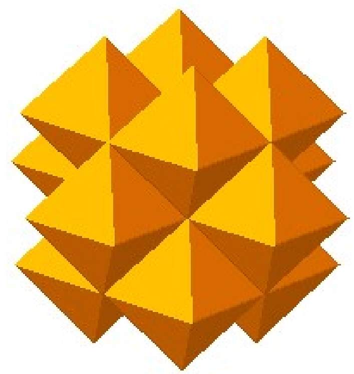

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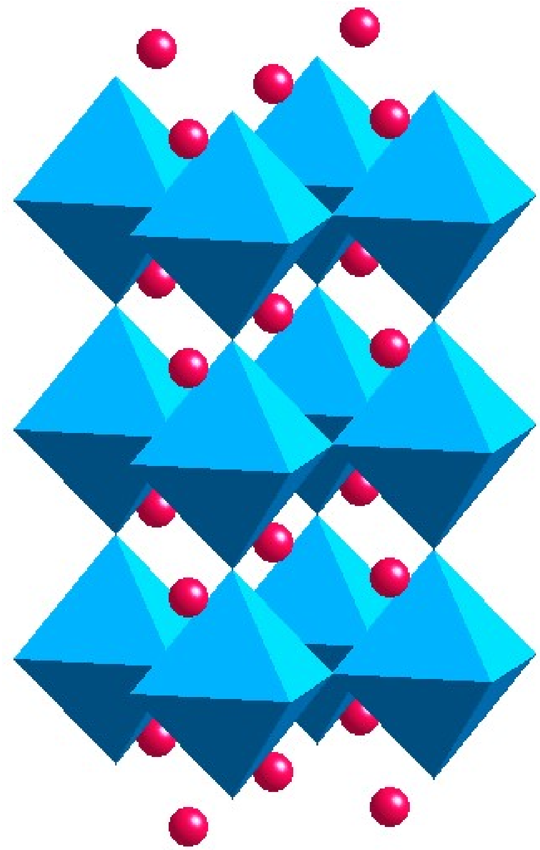
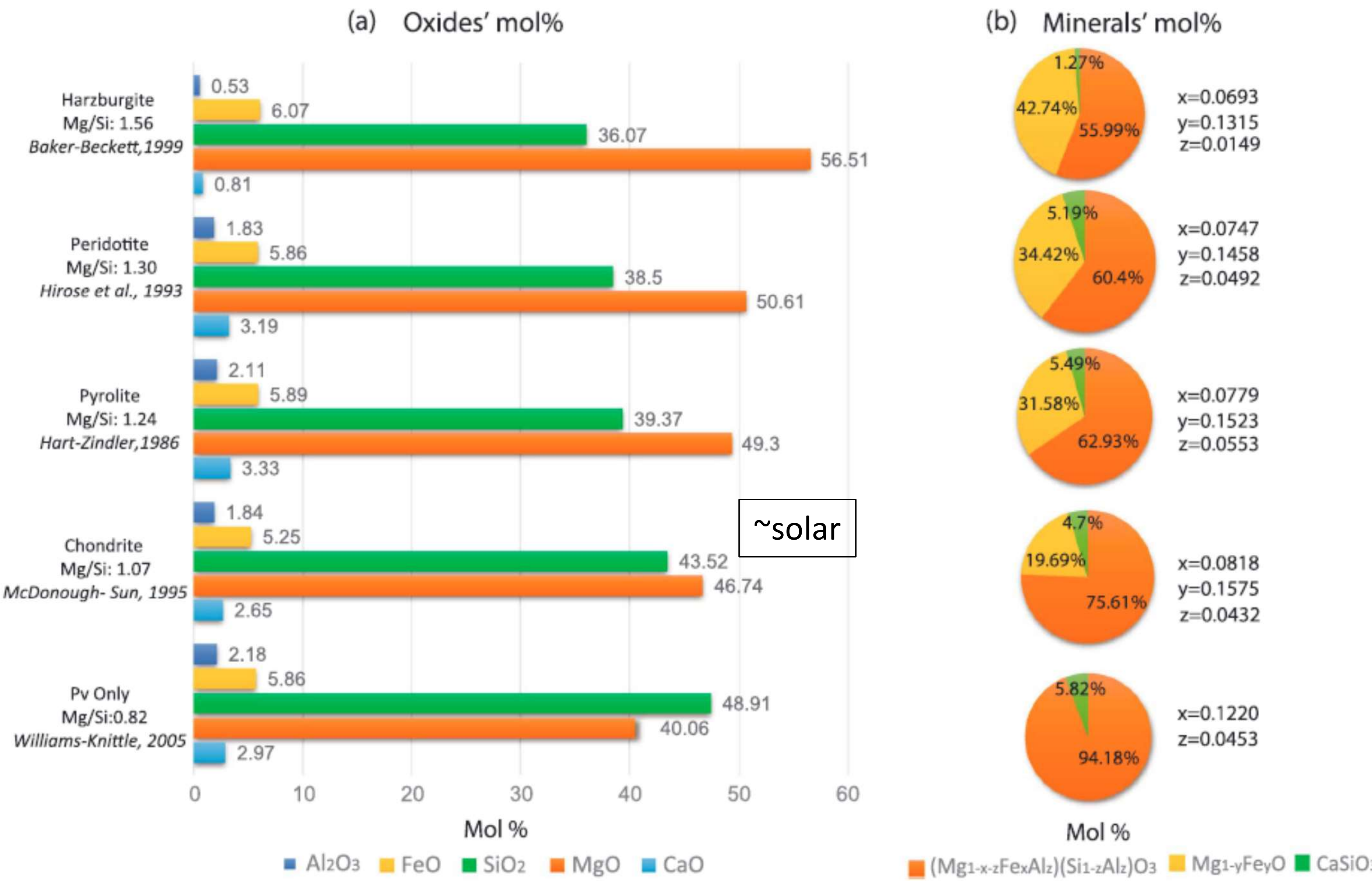


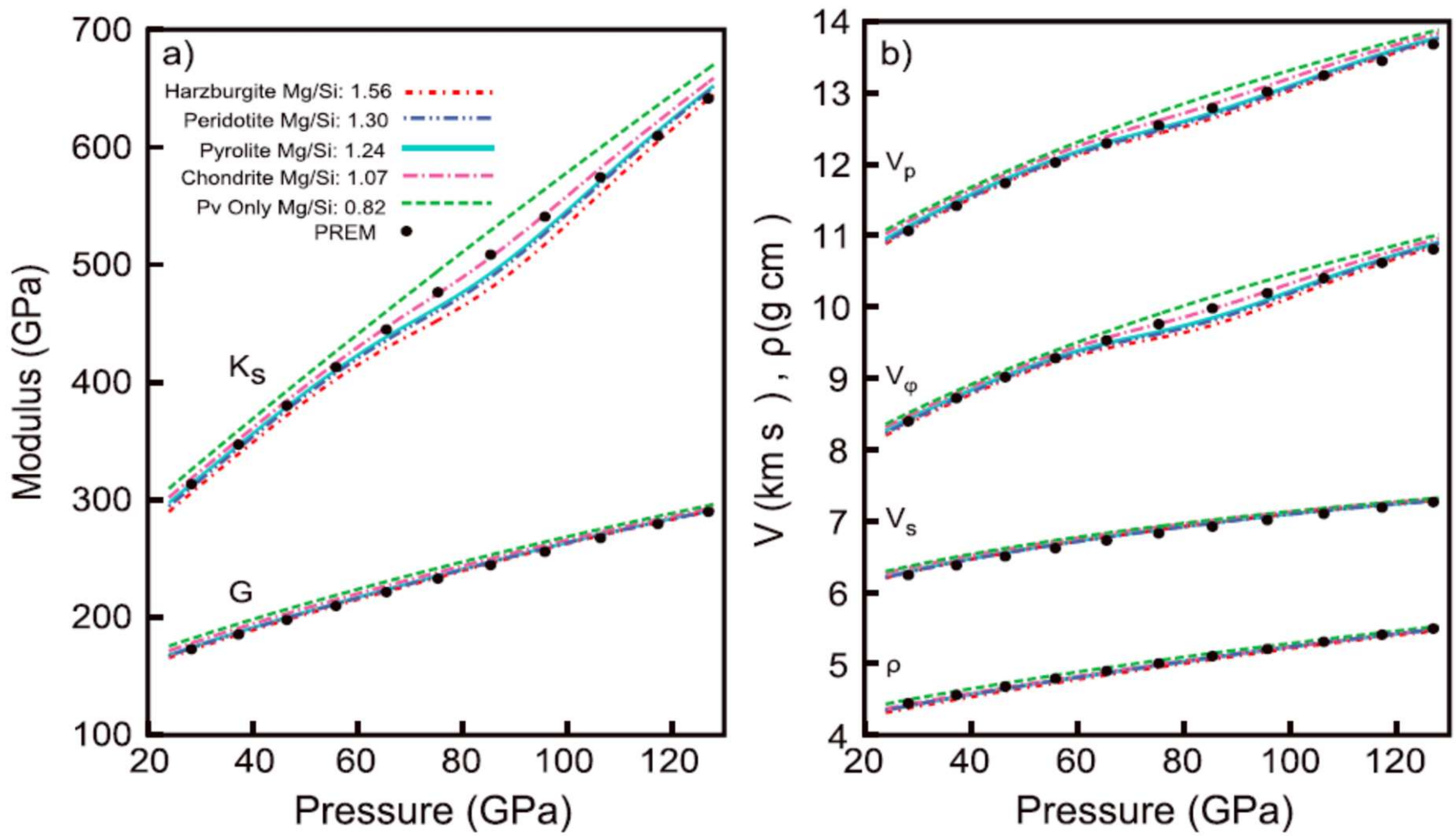
$(Mg_{(1-x-z)},Fe_x, Al_z)(Si_{(1-y)},Al_y)O_3$

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

$CaSiO_3$

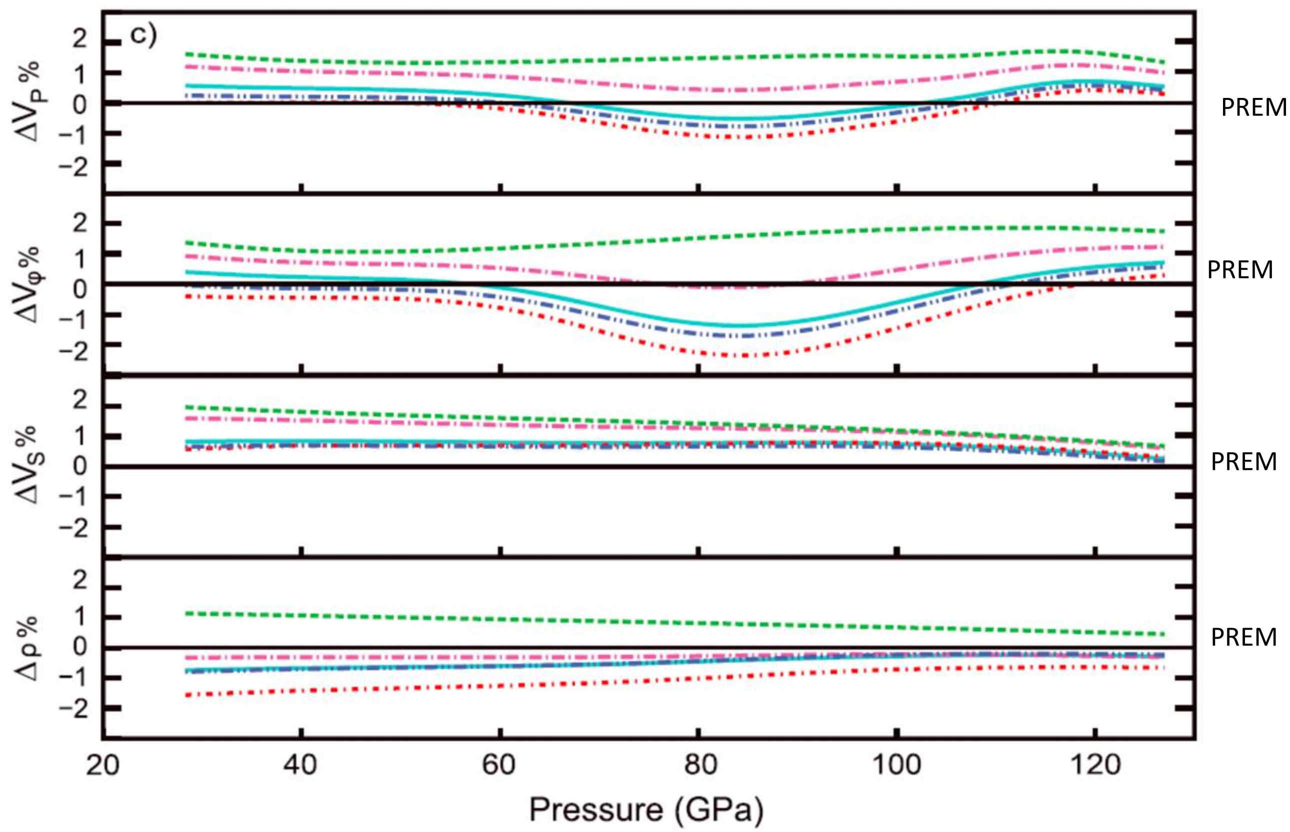

(a) Oxides' mol%
Harzburgite
Mg/Si: 1.56
Baker-Beckett,1999
0.53
6.07
36.07
56.51
0.81
Peridotite
Mg/Si: 1.30
Hirose et al., 1993
1.83
5.86
38.5
50.61
3.19
Pyrolite
Mg/Si: 1.24
Hart-Zindler,1986
2.11
5.89
39.37
49.3
3.33
Chondrite
Mg/Si: 1.07
McDonough- Sun, 1995
1.84
5.25
43.52
46.74
2.65
~solar
Pv Only
Mg/Si:0.82
Williams-Knittle, 2005
2.18
5.86
48.91
40.06
2.97
0
10
20
30
40
50
60
Mol %
Al_2O_3
FeO
SiO_2
MgO
CaO
(b) Minerals' mol%
1.27%
42.74%
55.99%
x=0.0693
y=0.1315
z=0.0149
5.19%
34.42%
60.4%
x=0.0747
y=0.1458
z=0.0492
5.49%
31.58%
62.93%
x=0.0779
y=0.1523
z=0.0553
4.7%
19.69%
75.61%
x=0.0818
y=0.1575
z=0.0432
5.82%
94.18%
x=0.1220
z=0.0453
Mol %
$(Mg_{1-x-z}Fe_xAl_z)(Si_{1-z}Al_z)O_3$
$Mg_{1-y}Fe_yO$
$CaSiO_3$

Can we see the spin crossover in Fp in the lower mantle?



Valencia-Cardona et al., GRL 2017

Can we see spin transition in the lower mantle?

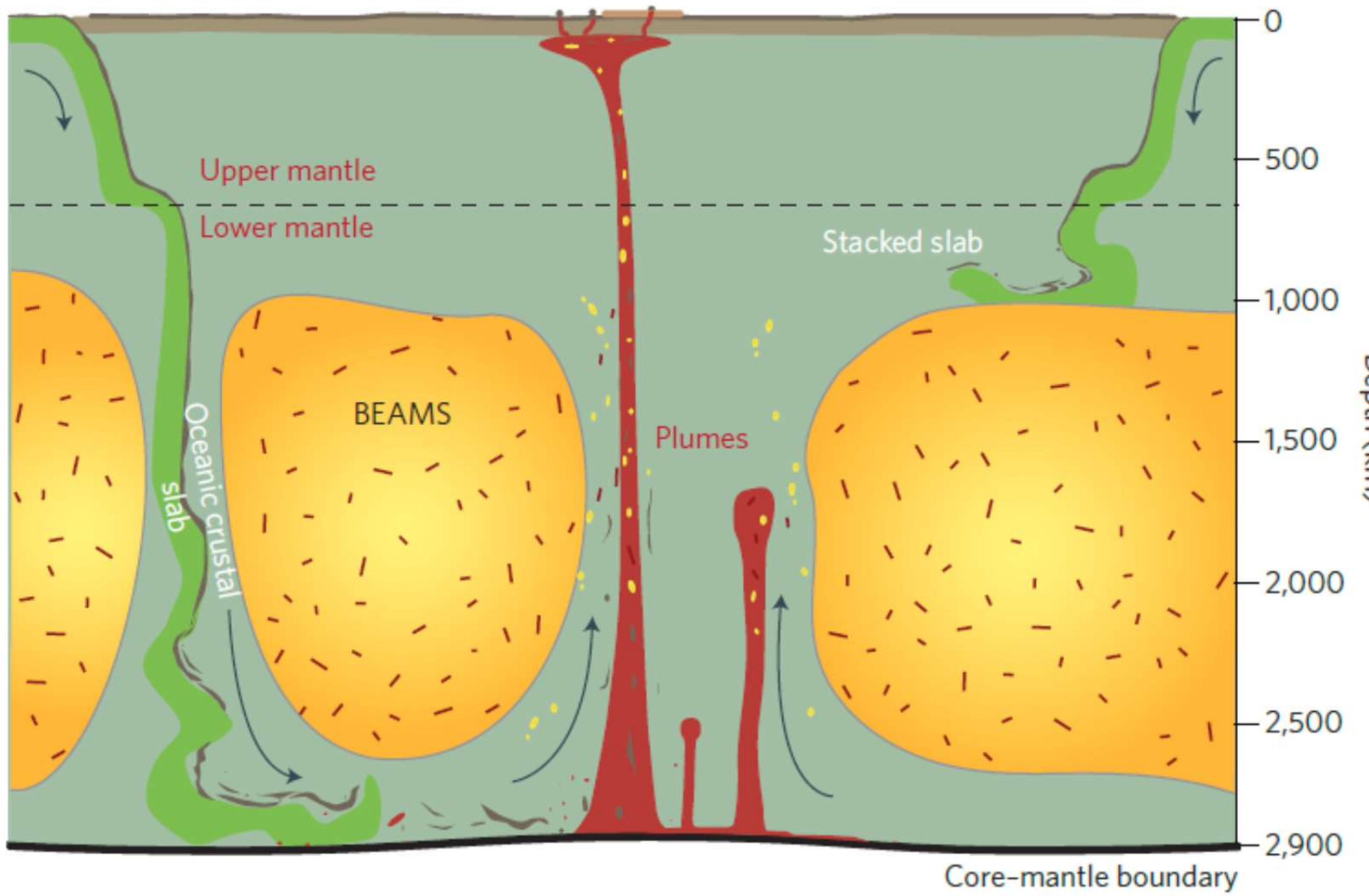


$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\alpha_{agg} V_{agg} T}{C_{p_{agg}}}$$

Valencia-Cardona et al., GRL 2017

Bridgmanite Enriched Mantle Structures can survive convection in the lower mantle

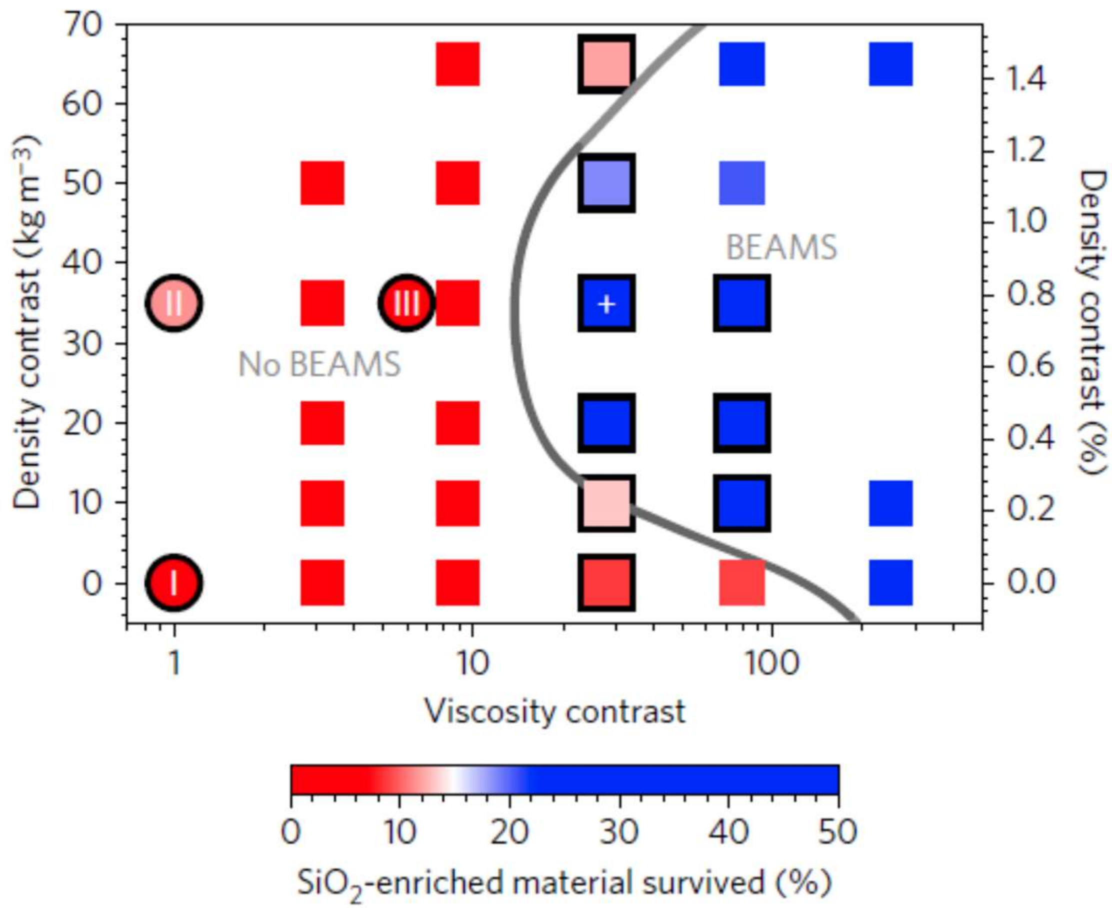
BEAMS



Ballmer, Houser, Hernlund, Wentzcovitch, Hirose, Nat. Geosc. 2017

Bridgmanite Enriched Mantle Structures can survive convection in the lower mantle

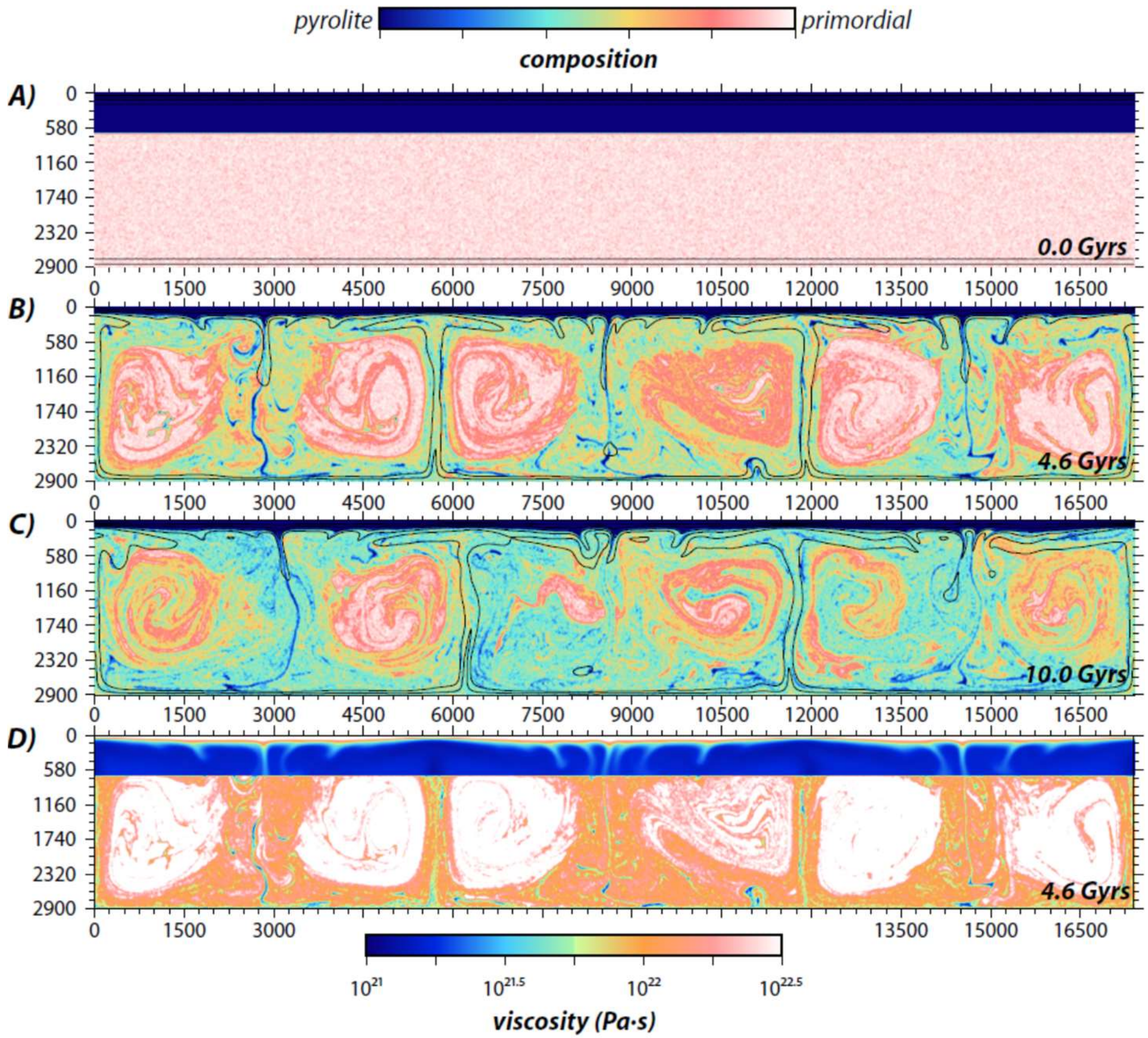
BEAMS



Ballmer, Houser, Hernlund, Wentzcovitch, Hirose, Nat. Geosc. 2017

Bridgmanite Enriched Mantle Structures can survive convection in the lower mantle

BEAMS



Ballmer, Houser, Hernlund, Wentzcovitch, Hirose, Nat. Geosc. 2017

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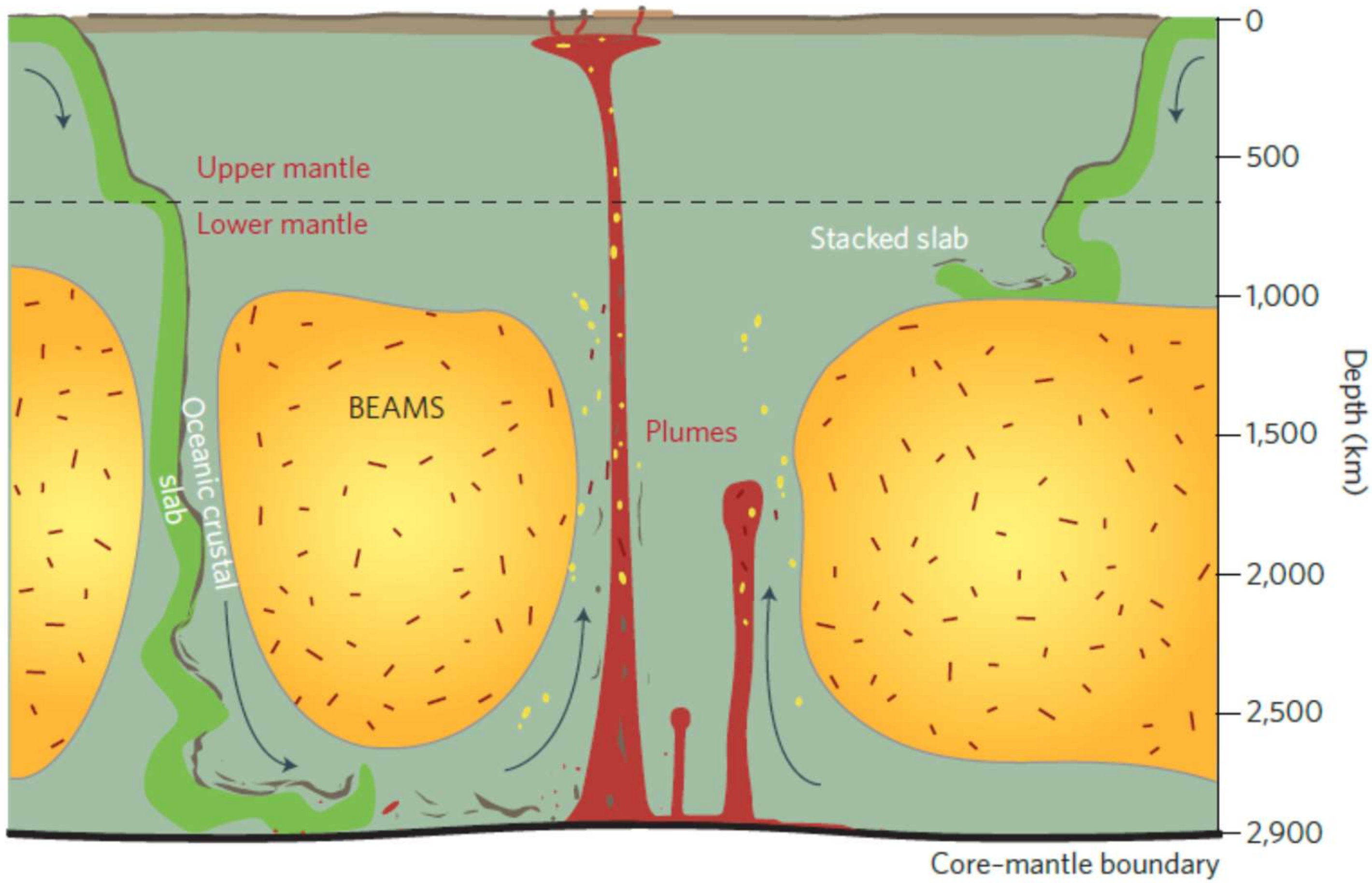
BEAMS

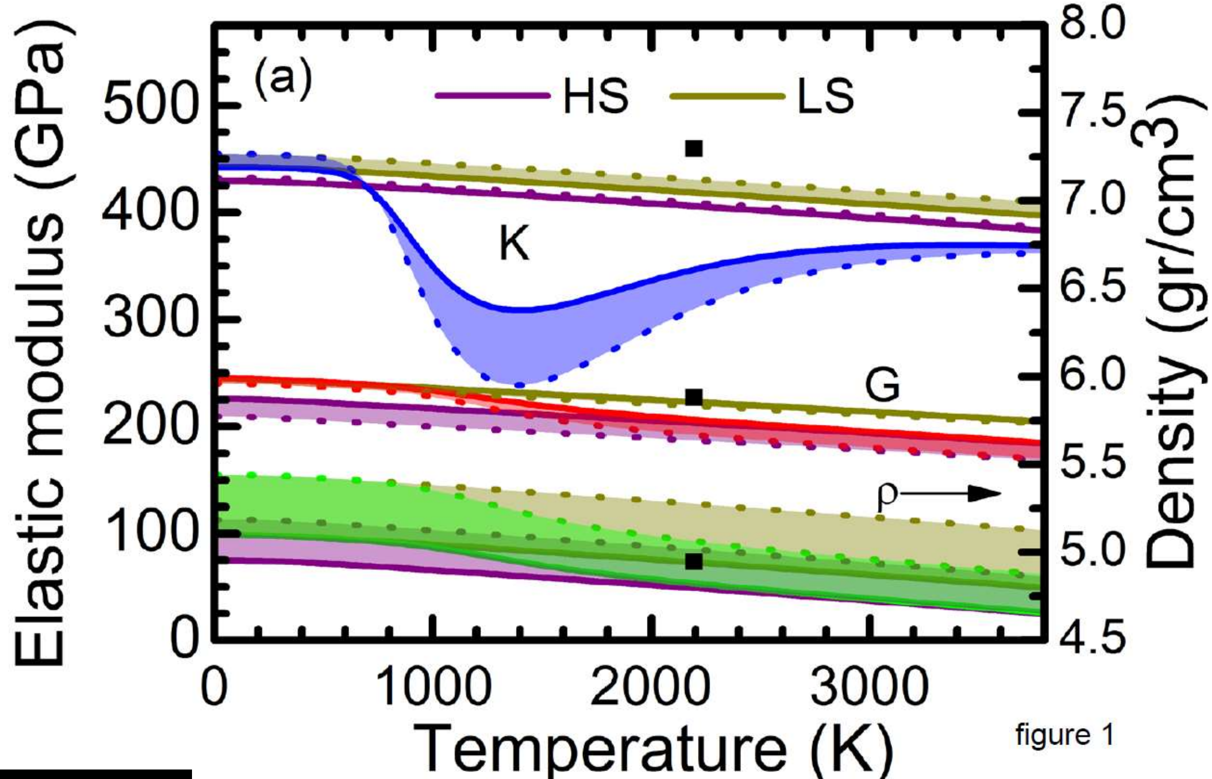


Ballmer, Houser, Hernlund, Wentzcovitch, Hirose, Nat. Geo. 2017

But, can we see spin crossover in the lower mantle?

Elastic anomalies in ferropericlase - II

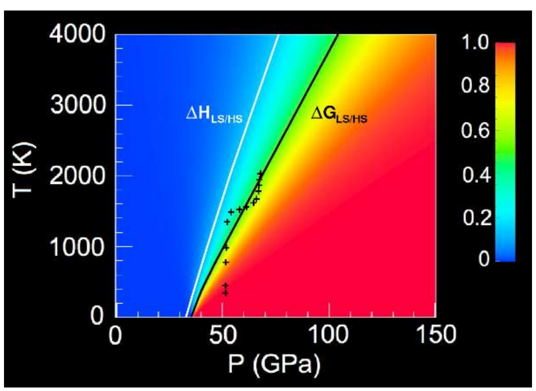
Wu and Wentzcovitch, PNAS 2014



P = 75 GPa

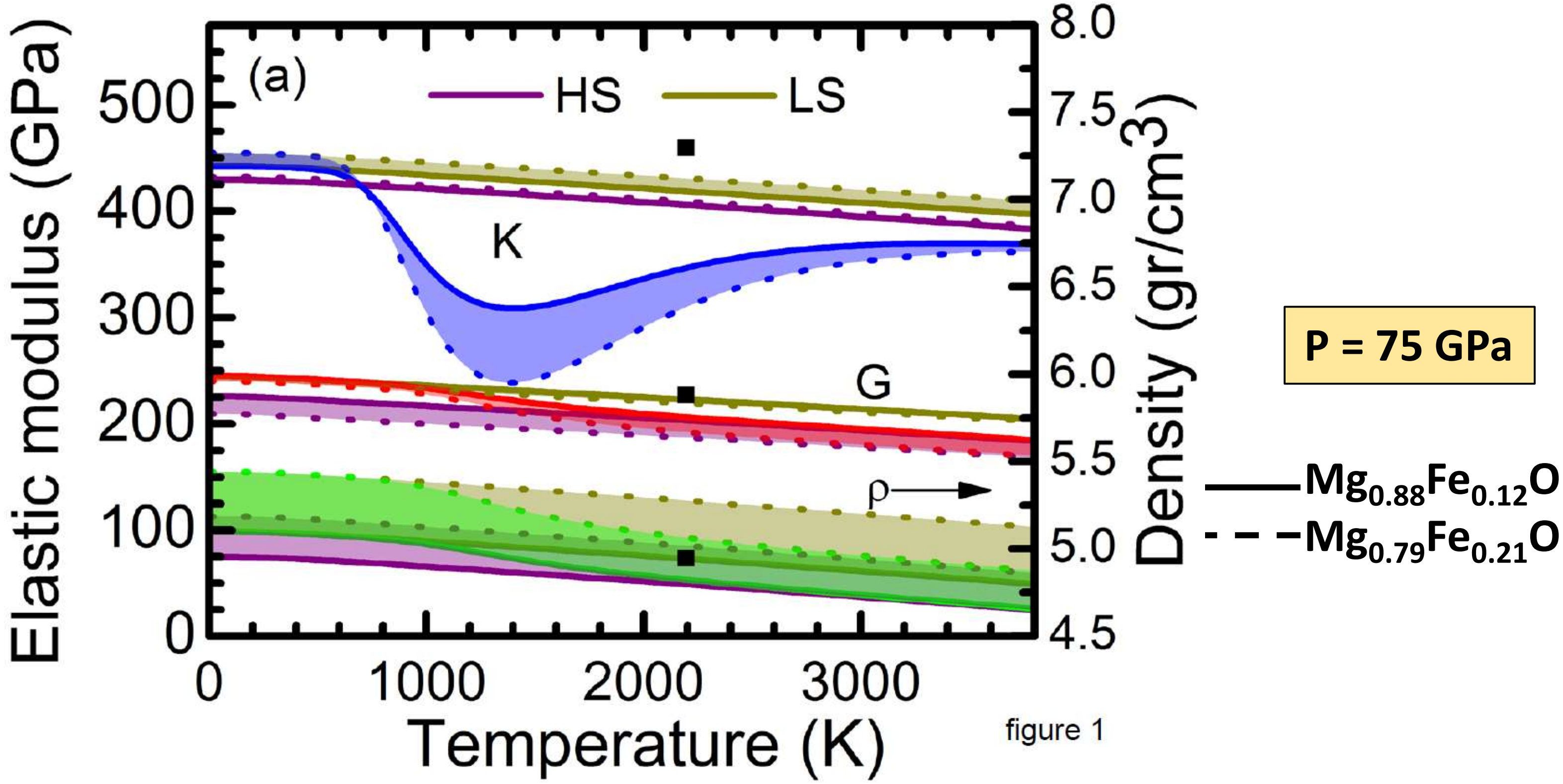
—— $Mg_{0.88}Fe_{0.12}O$

– – – $Mg_{0.79}Fe_{0.21}O$



Elastic anomalies in ferropericlase - II

Wu and Wentzcovitch, PNAS 2014

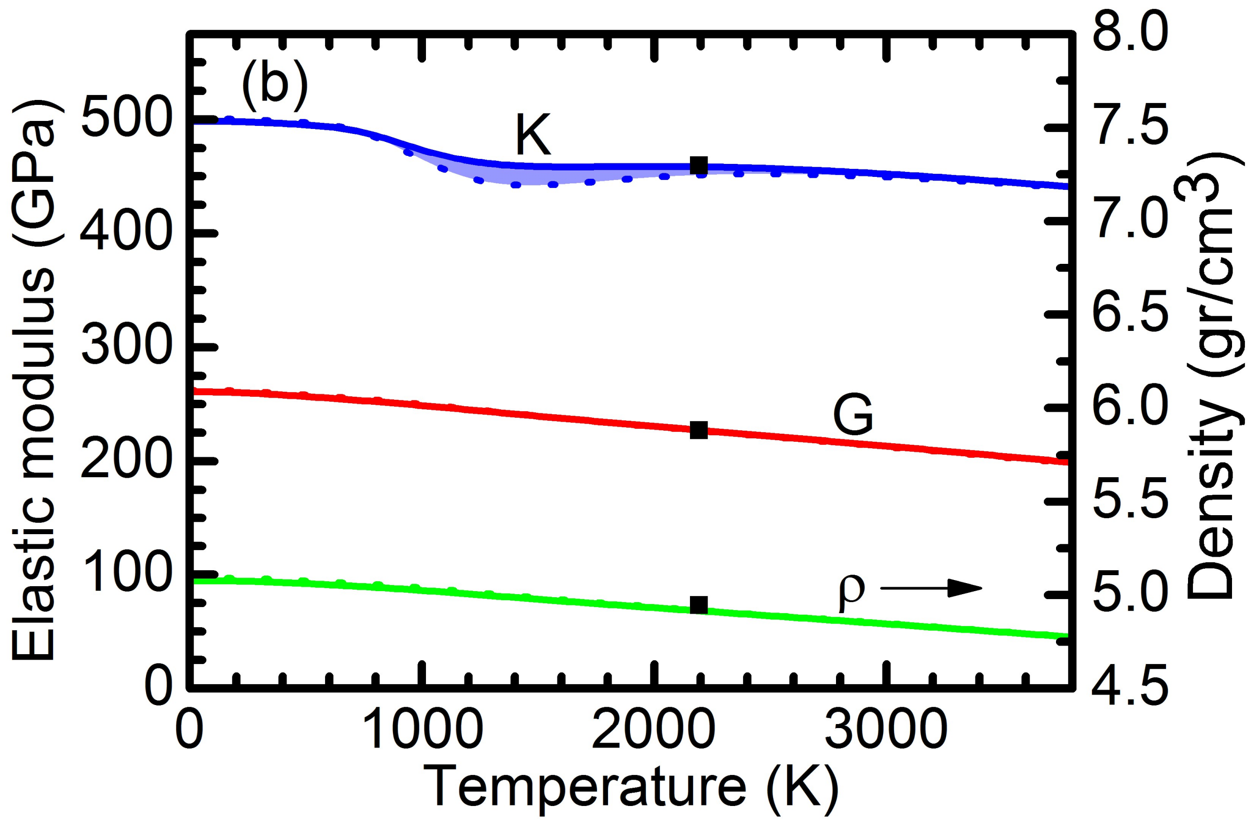


$$V_P = \sqrt{\frac{K_S + \frac{3}{4}G}{\rho}}$$

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

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% $Mg_{0.88}Fe_{0.12}O$

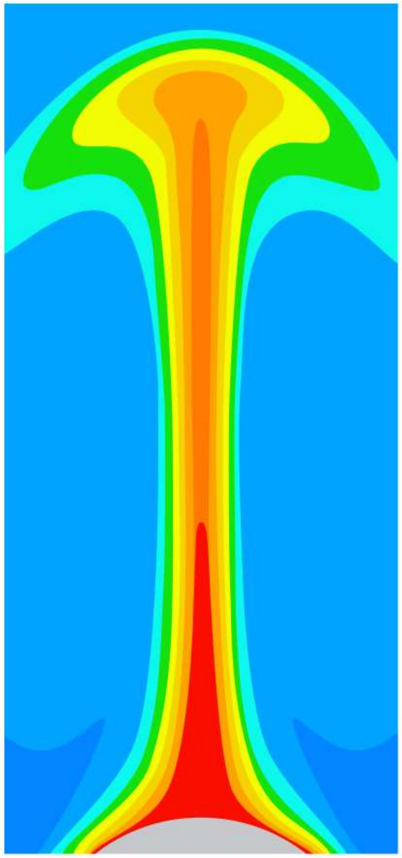
- - - 78% $(Mg_{0.91}Fe_{0.09})SiO_3$ (MgPv) + 7% $CaSiO_3$ + 15% $Mg_{0.79}Fe_{0.21}O$

Predicted effect

Wu and Wentzcovitch, PNAS 2014

Slow (hot) anomaly (plume) with spin crossover

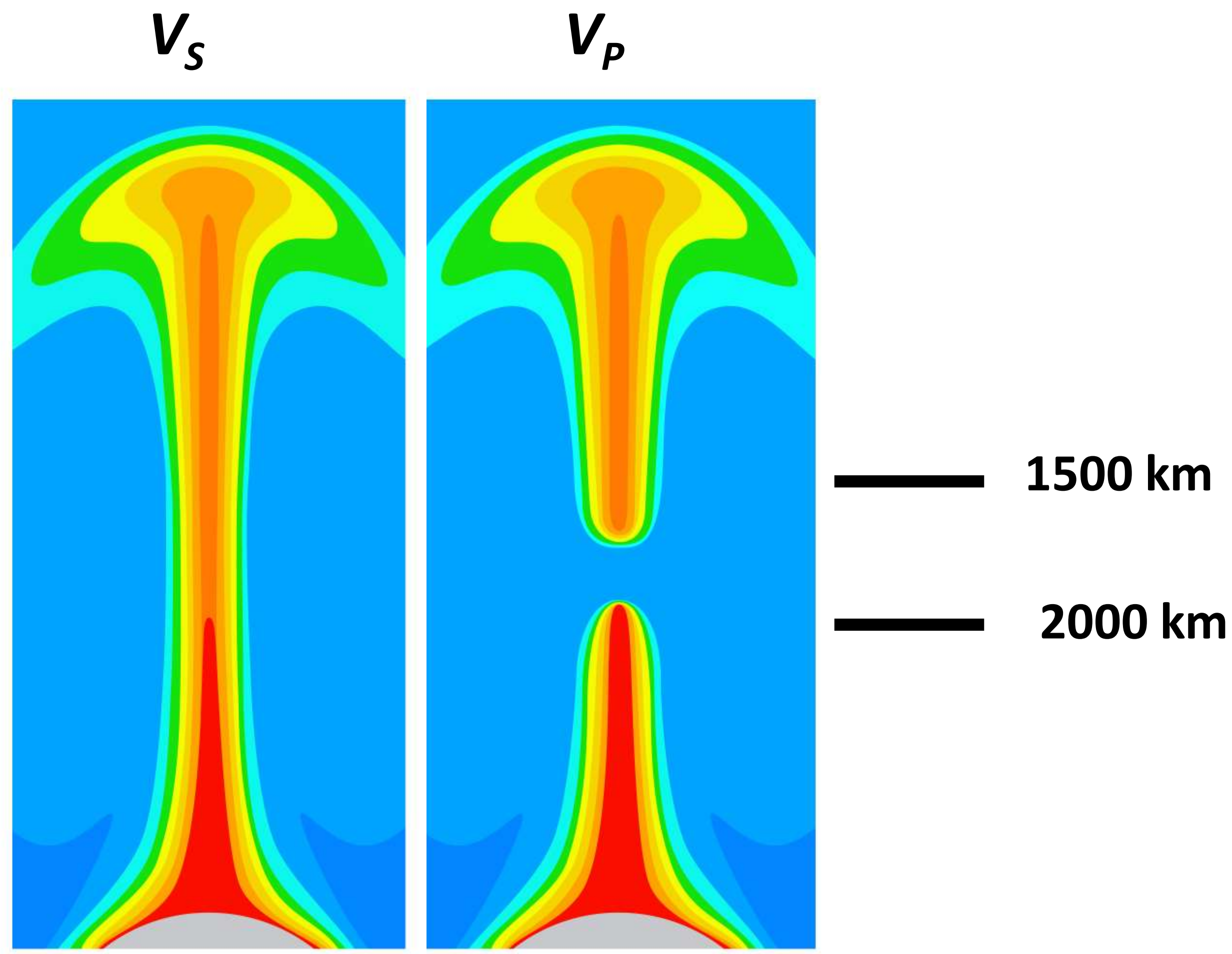
V_S



Predicted effect

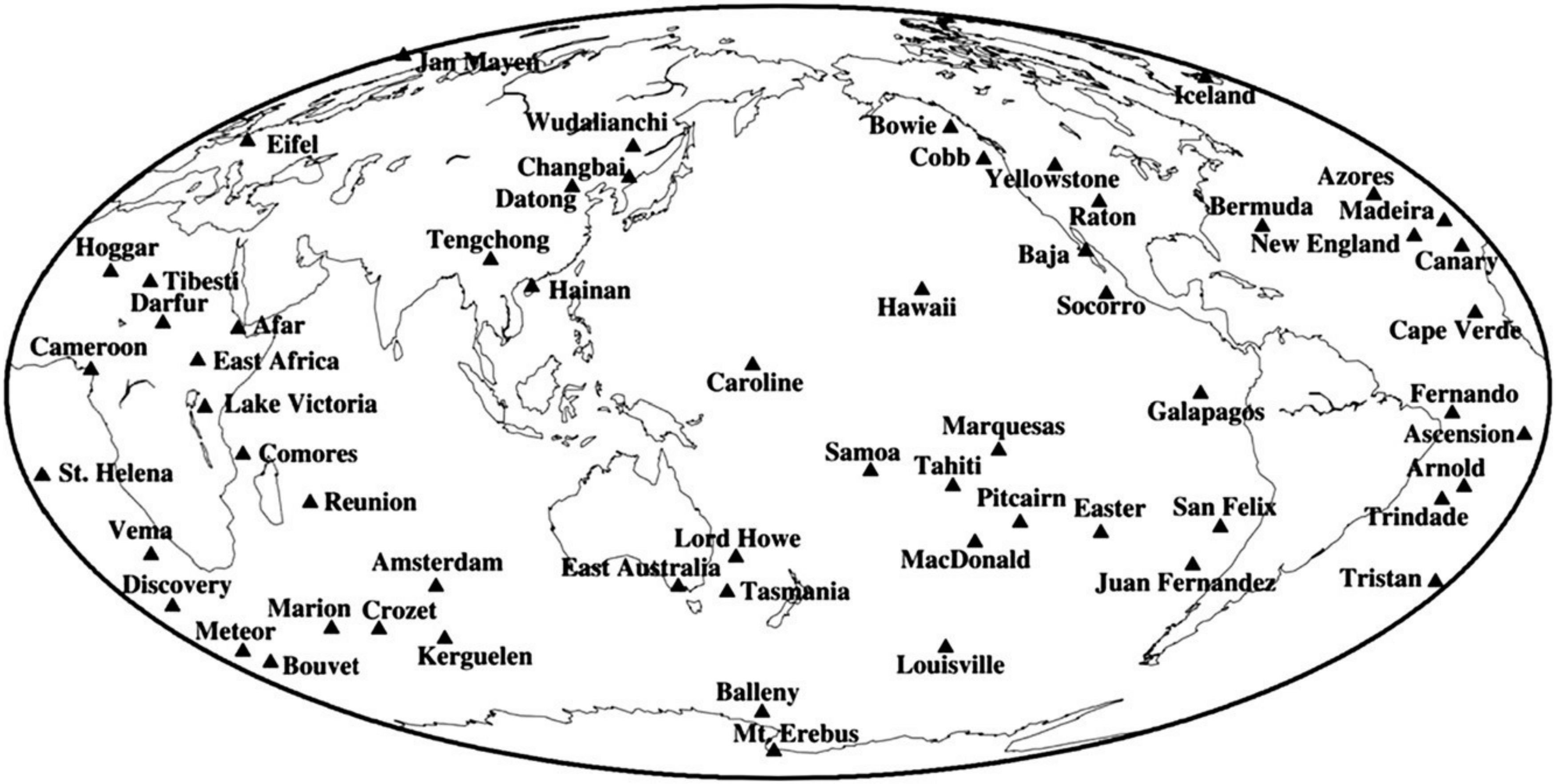
Wu and Wentzcovitch, PNAS 2014

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



Potential seismic signatures of spin crossover

Wu and Wentzcovitch, PNAS 2014

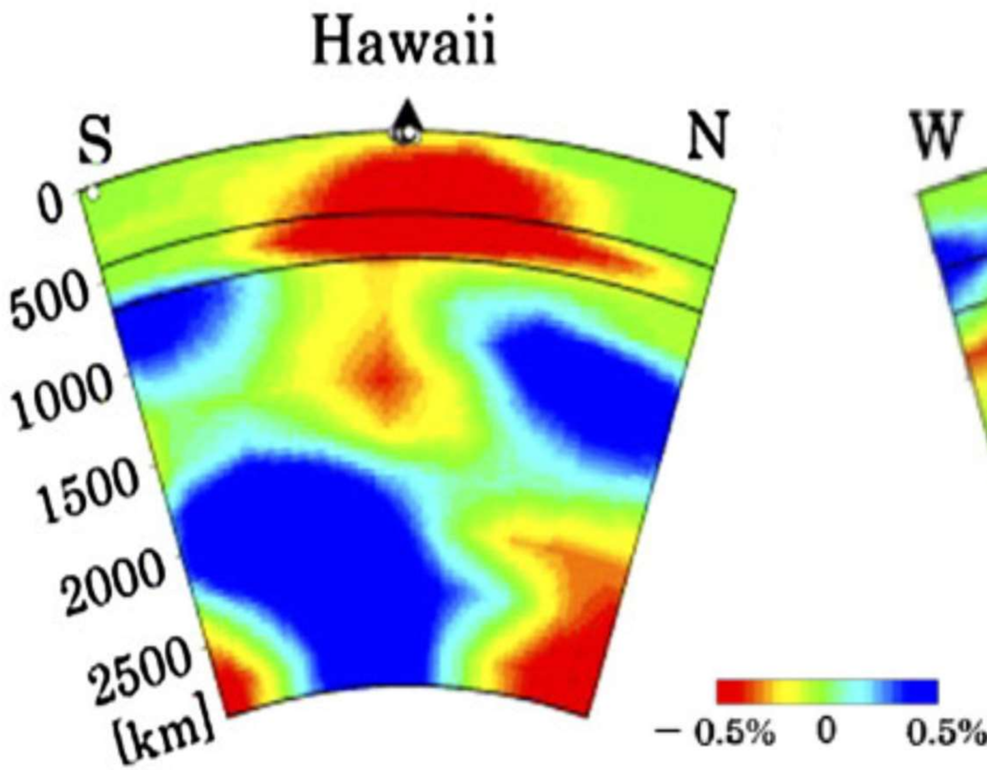


P-models

Zhao, Gondwana Res. 2007

Potential seismic signatures of a spin crossover

Wu and Wentzcovitch, PNAS 2014

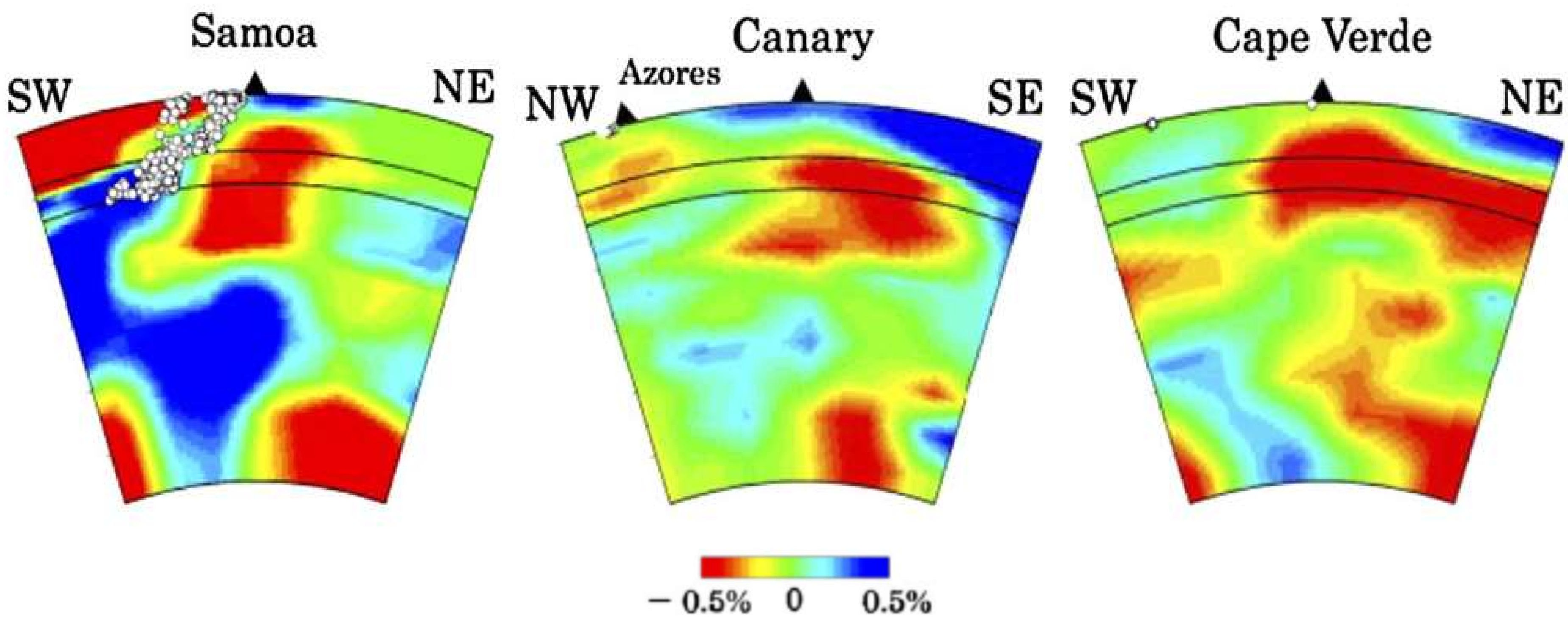


Zhao, Gondwana Res. 2007

P-models

Potential seismic signatures of spin crossover

Wu and Wentzcovitch, PNAS 2014



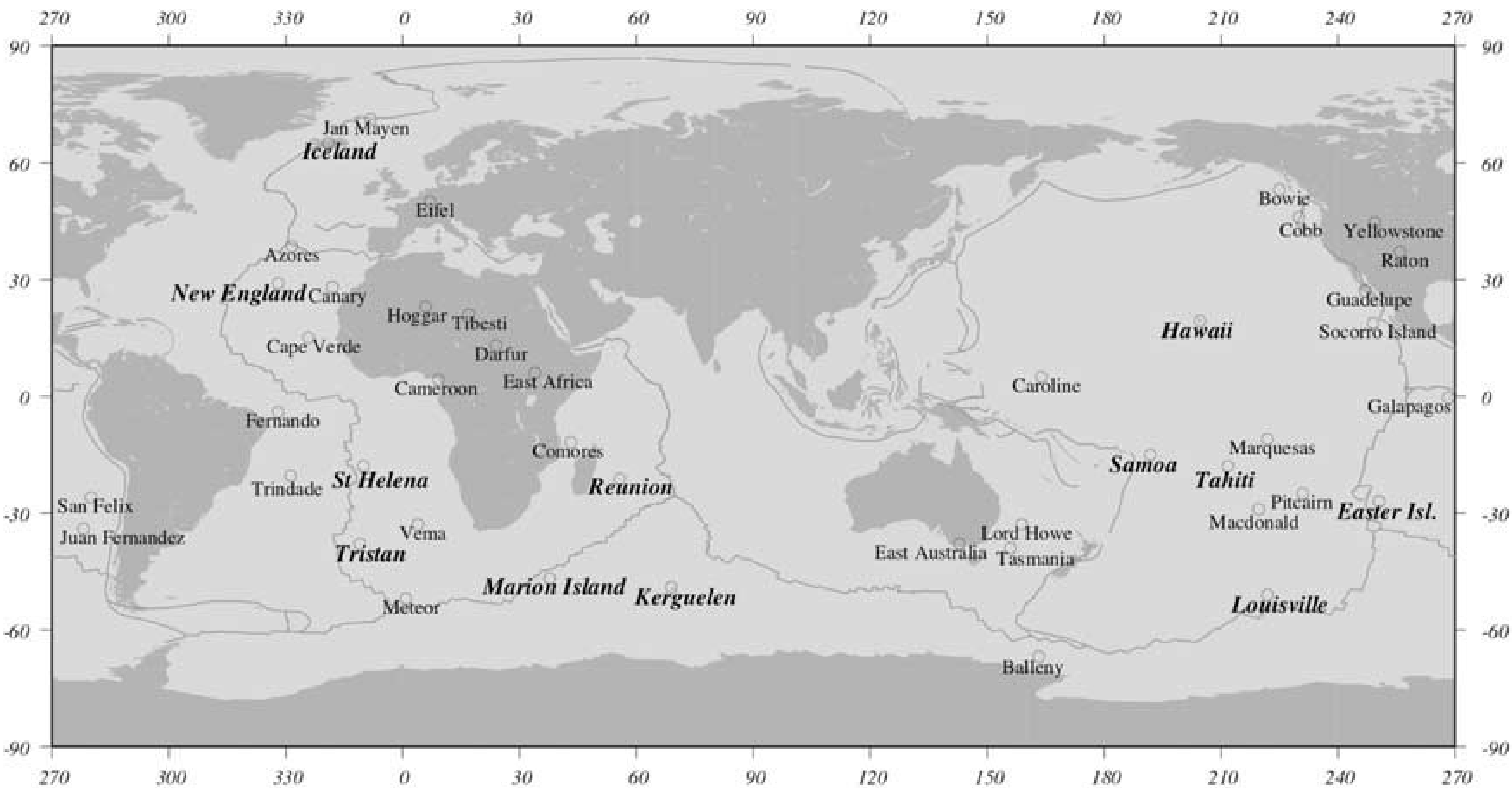
Zhao, Gondwana Res. 2007

P-models

Geodynamic/seismological analysis of global models

Boschi, Becker, Steinberger, G^3, 2007

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

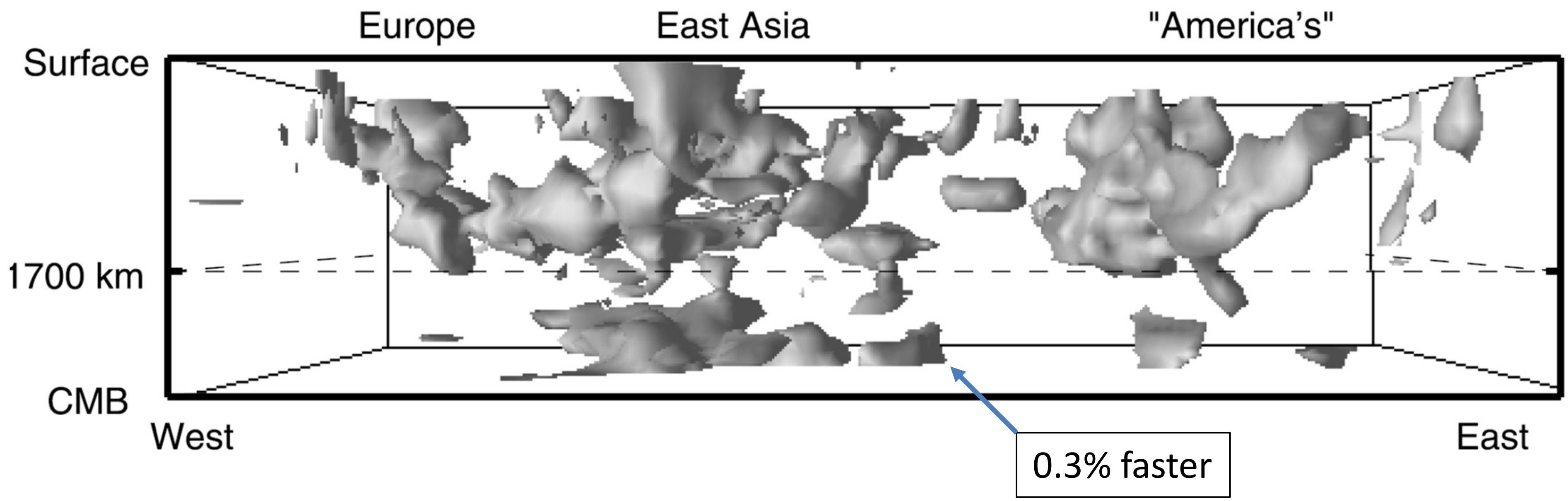


Compositional Heterogeneity in the Bottom 1000 Kilometers of Earth's Mantle: Toward a Hybrid Convection Model

Science AAAS

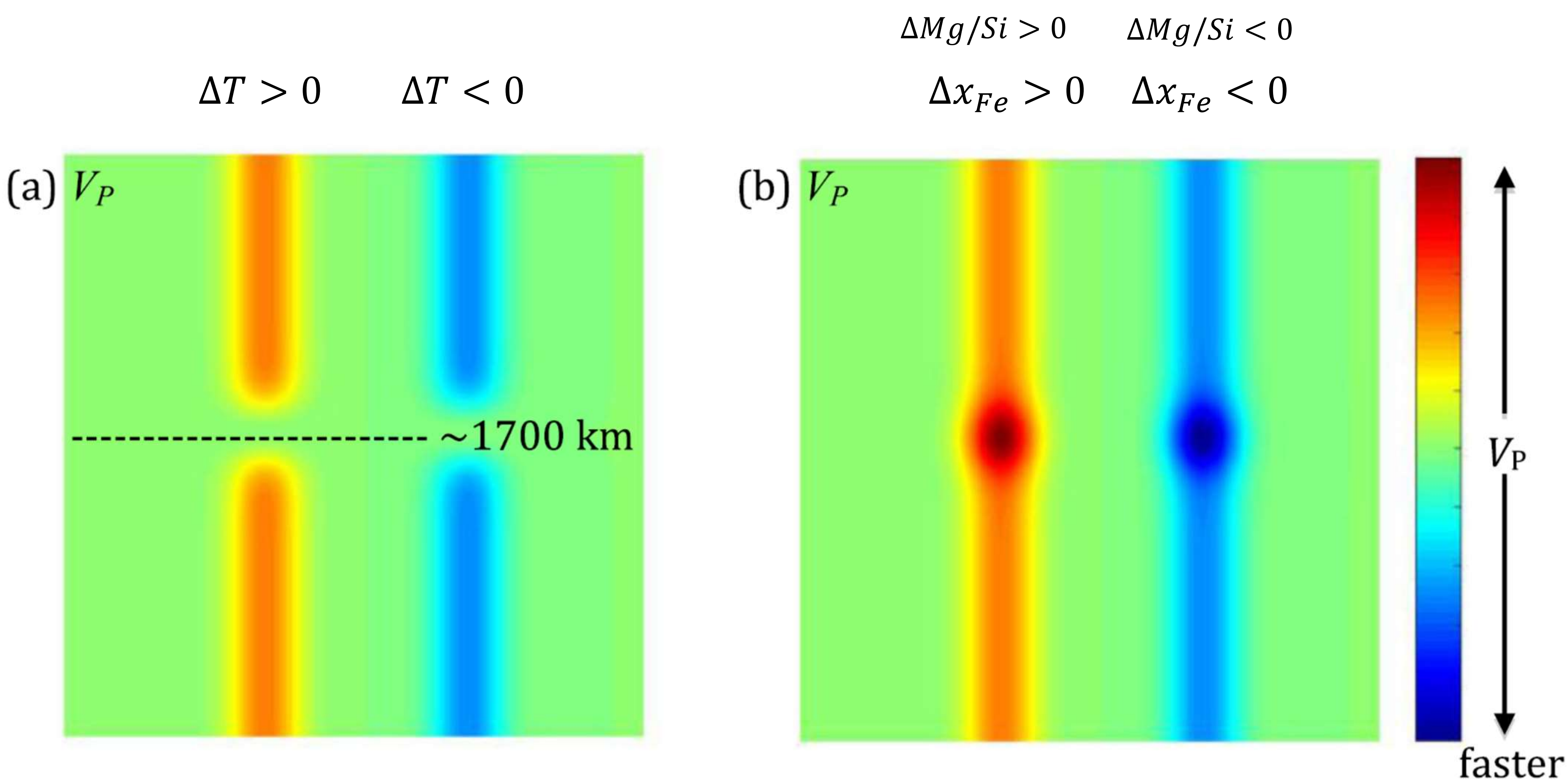
1999

Rob D. van der Hilst* and Hrafnkell Kárason



P-model

Thermal and chemical heterogeneities



Chemically homogeneous

Laterally isothermic

Can we see spin transition in the lower mantle?

- Absence of spin crossover signature in 1D models suggests the presence of silicate rich, high viscosity structures in the lower mantle (BEAMS)
- Signatures of spin crossover in Fp should be identifiable in tomographic models but co-existence with chemical heterogeneities complicates analyses of models
- Several hot spot plumes appear to display the pattern of P-heterogeneities predicted by a spin crossover in ferropericlase while S-heterogeneities do not.
- The pattern is consistent with predictions of heterogeneities caused by spin crossover in Fp

Thank you!!