Ab initio calculations on iron and iron alloys at Earth’s core conditions

Lidunka Vočadlo

Department of Earth Sciences, UCL

Can mineral physics match seismology?

Is there an inner core composition that has the same elastic properties (V_P, V_S) as the observation

Talk Outline

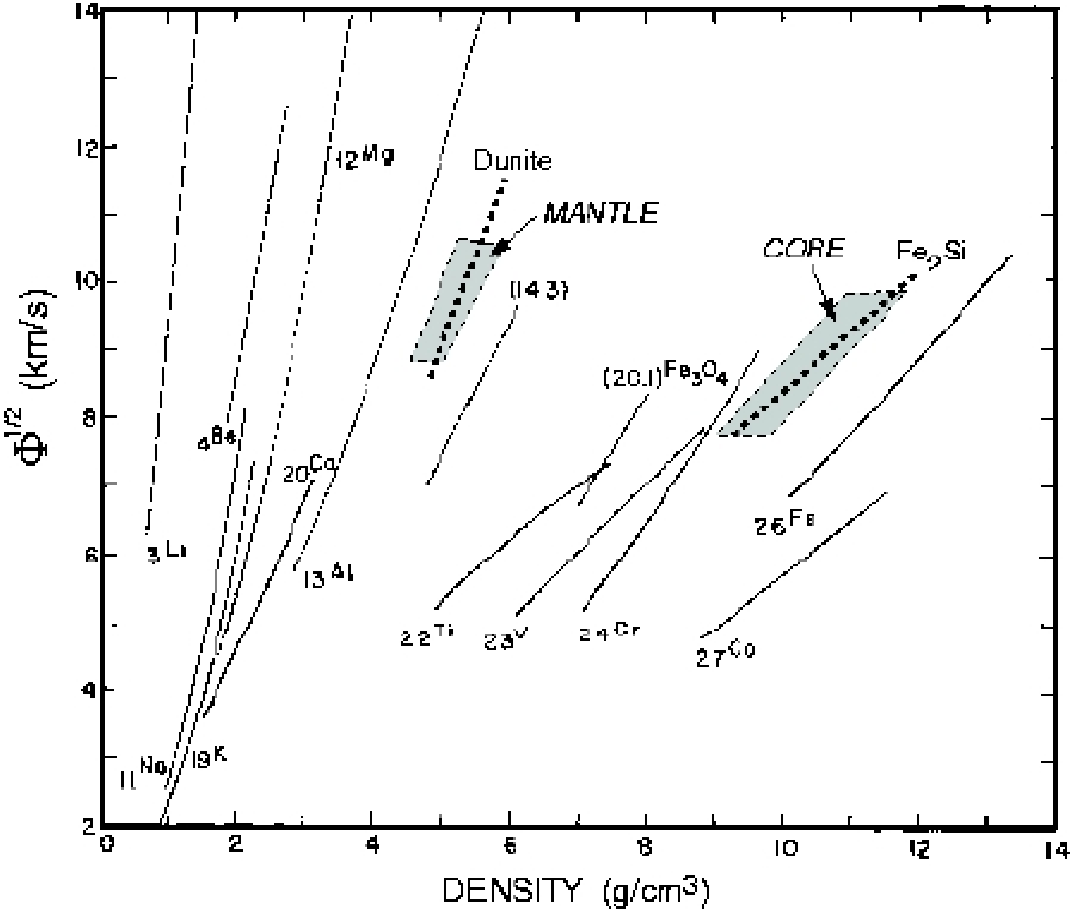
- Why is the core interesting?

- What are ab initio calculations?
  - Simulating pressure
  - Simulating temperature

- What composition matches seismology?
  - Pure iron phases
  - Effect of light elements
  - Effect of nickel

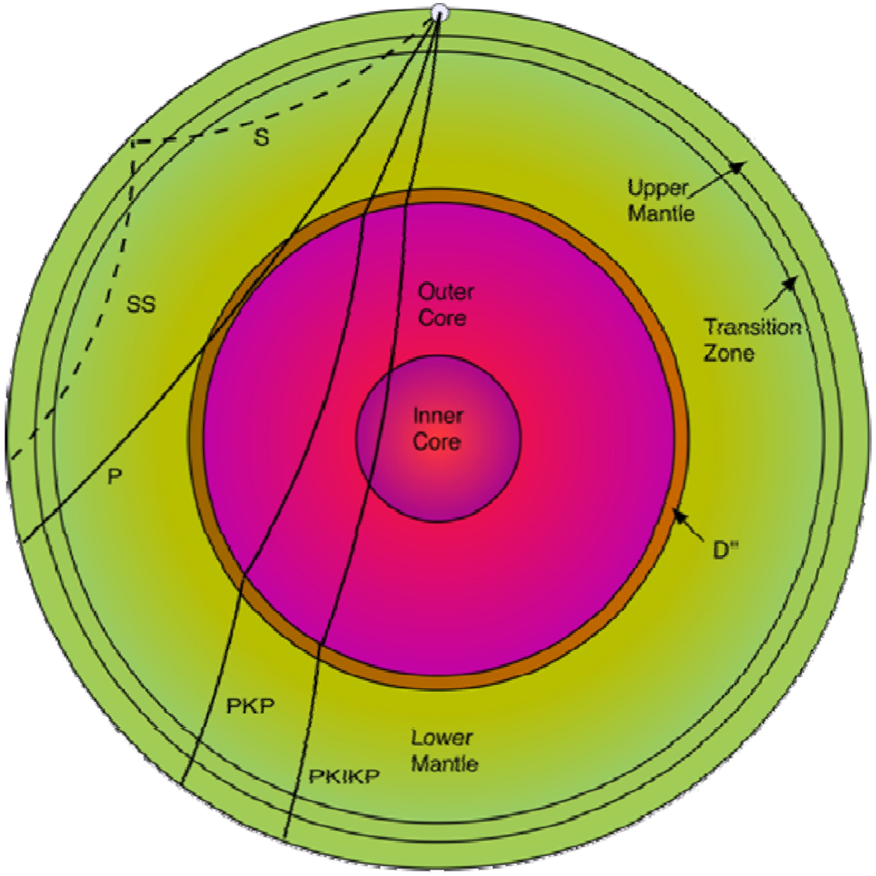
The Earth’s Core

Seismology tells us the core is close to pure Fe



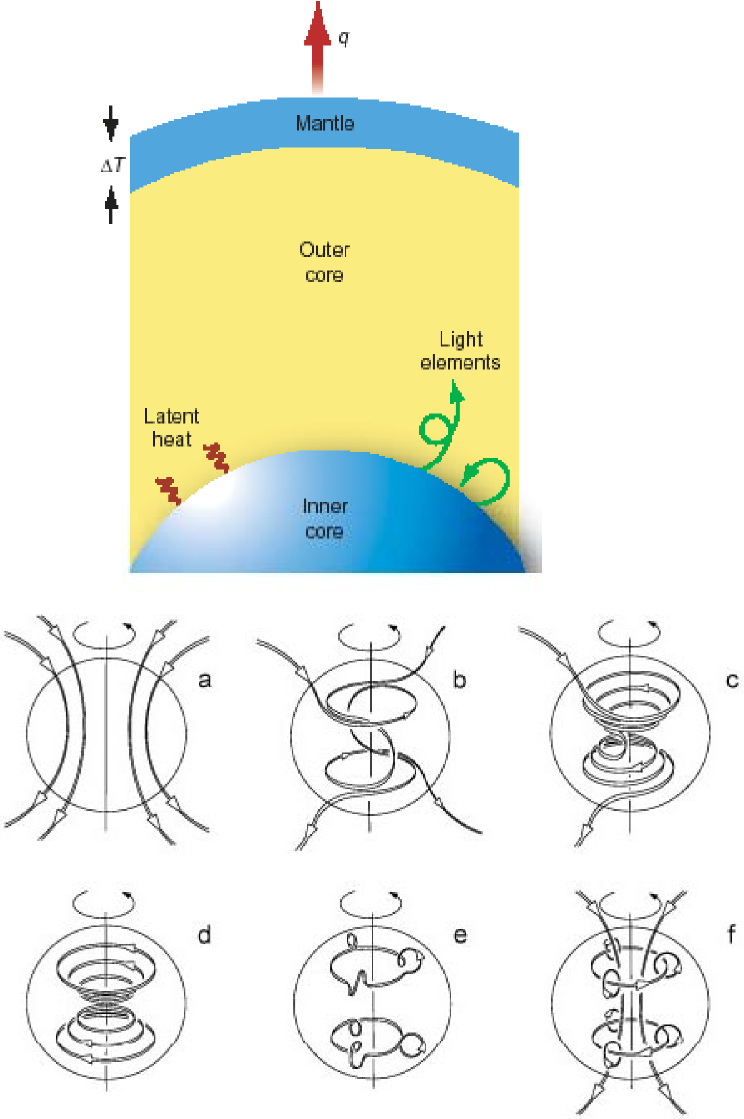
Francis Birch

The Earth’s Core: traditional view

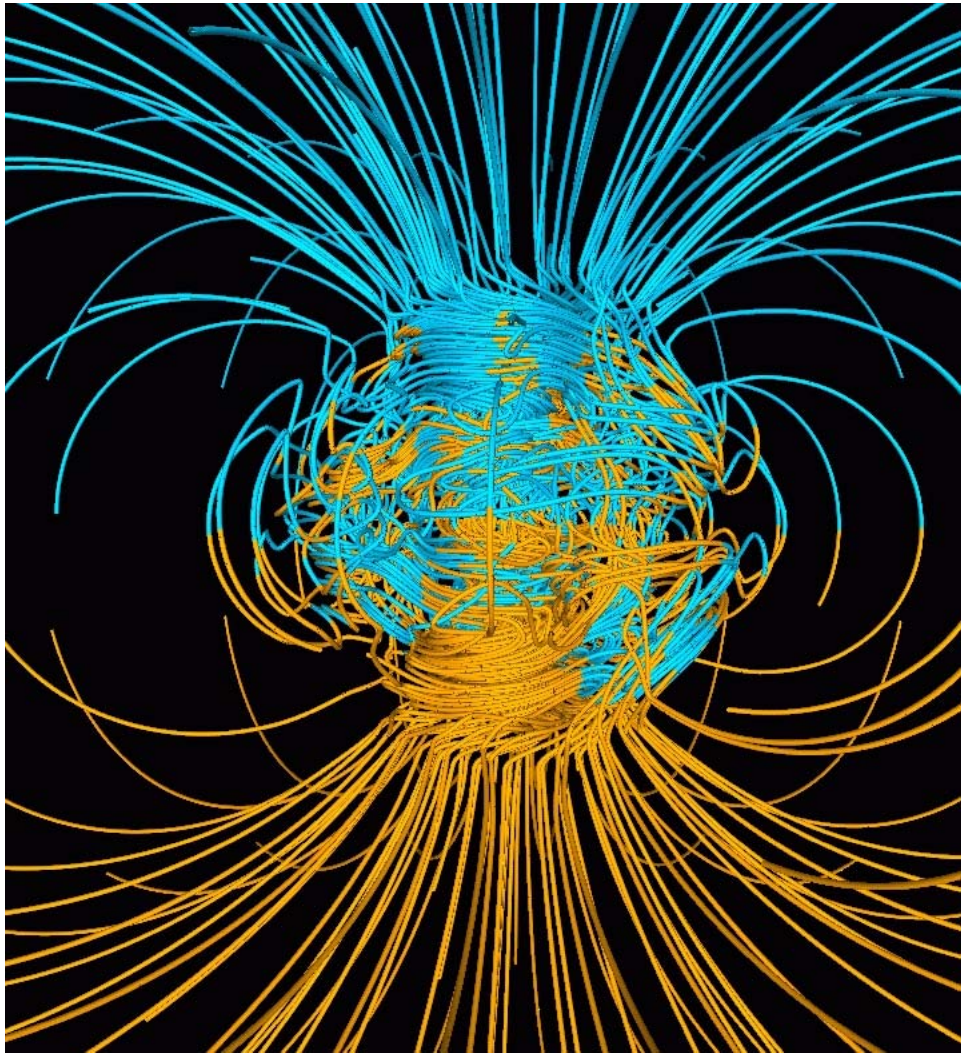


- The Earth’s core is mainly Fe with Ni and light elements
- The outer core is liquid and runny, ~10% less dense than Fe with T~4000-6000K
- The inner core is solid, 3-4% less dense than Fe
- IC is crystallising from the OC.
- Light alloying elements may be things like Si, S, O, C, H....

The outer core: the geodynamo

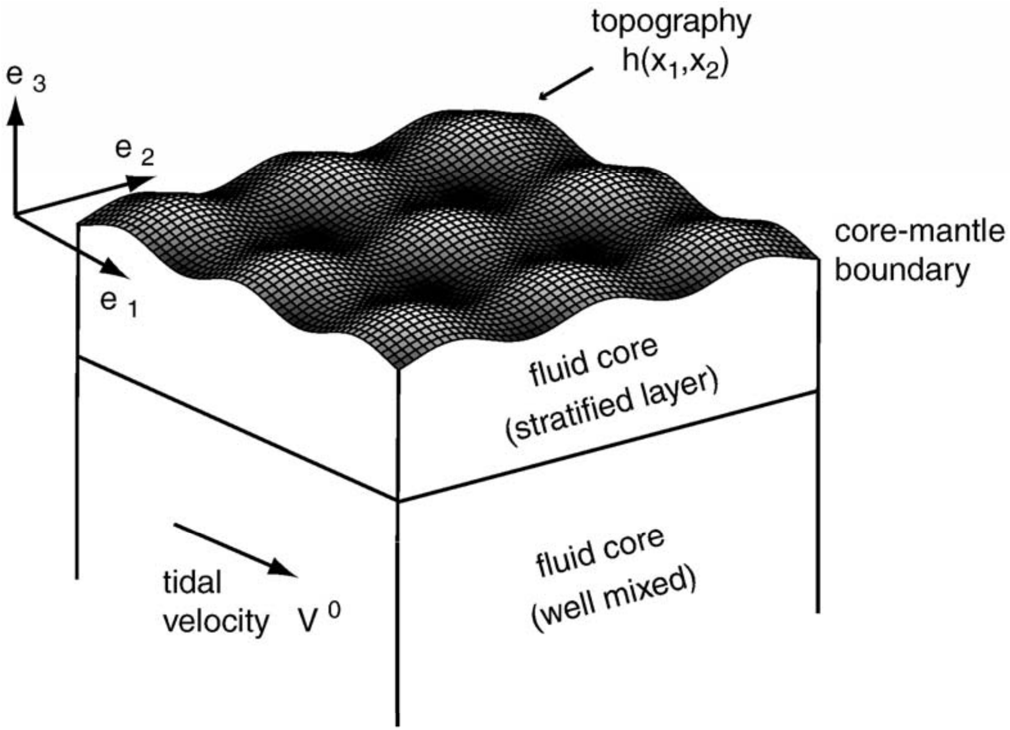


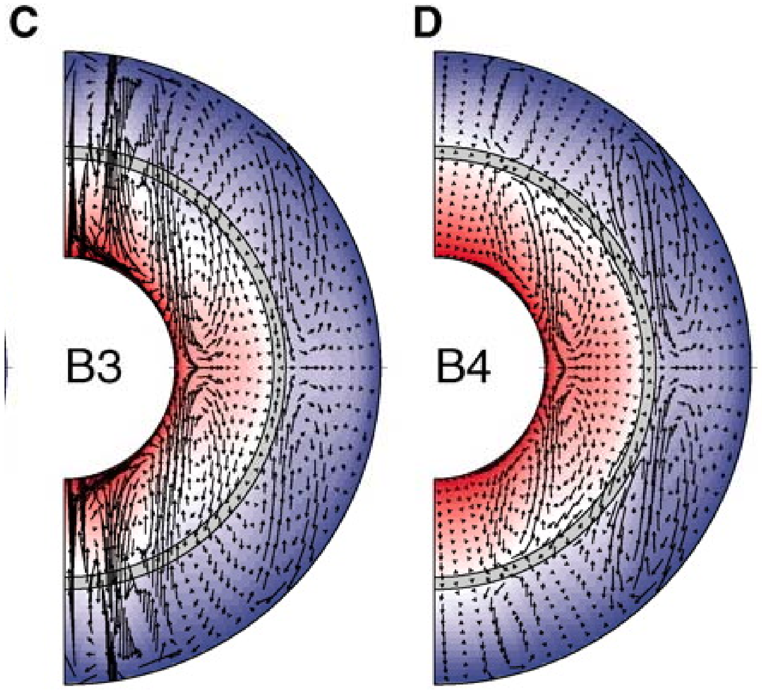
Love, J. J., 1999. Astronomy & Geophysics, 40, 6.14-6.19.



Glatzmaier and Roberts 1995

The outer core: stratification?



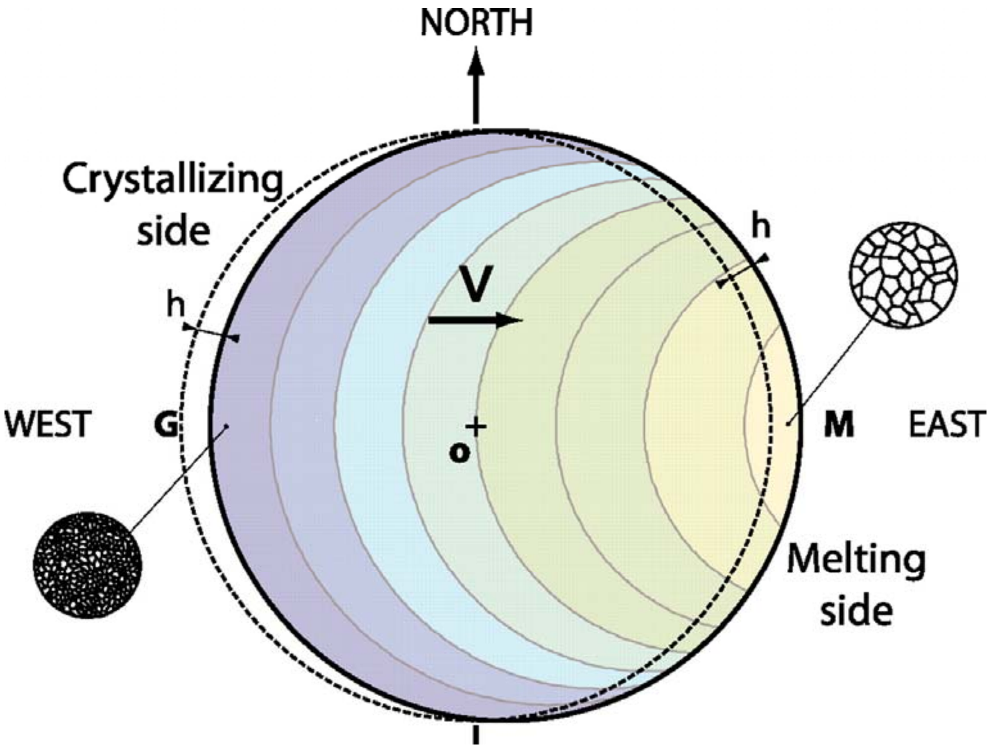


Buffett, EPSL, 2010

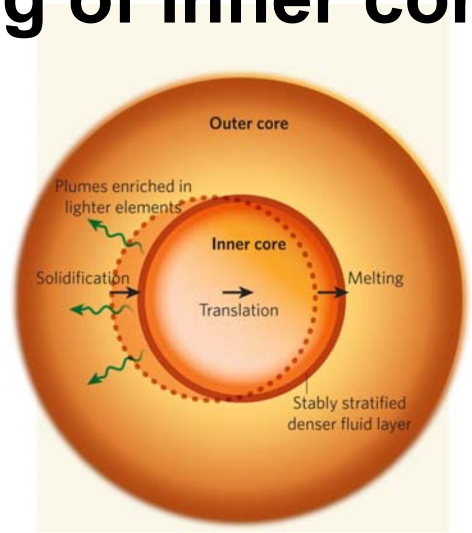
Ozawa et al., Science, 2011

Huang et al. rule out O altogether (Nature yesterday!)

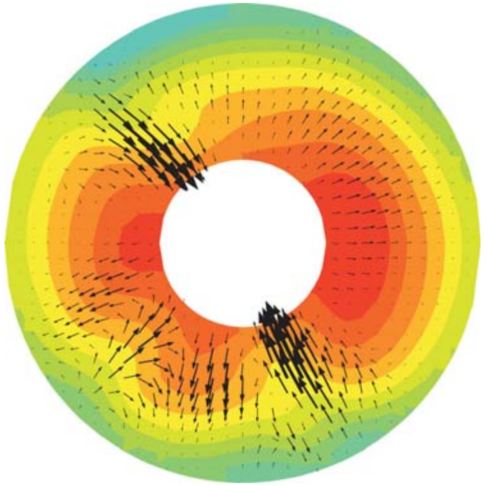
Hemispherical solidification/melting of inner core?



Monnereau et al., Science 2010

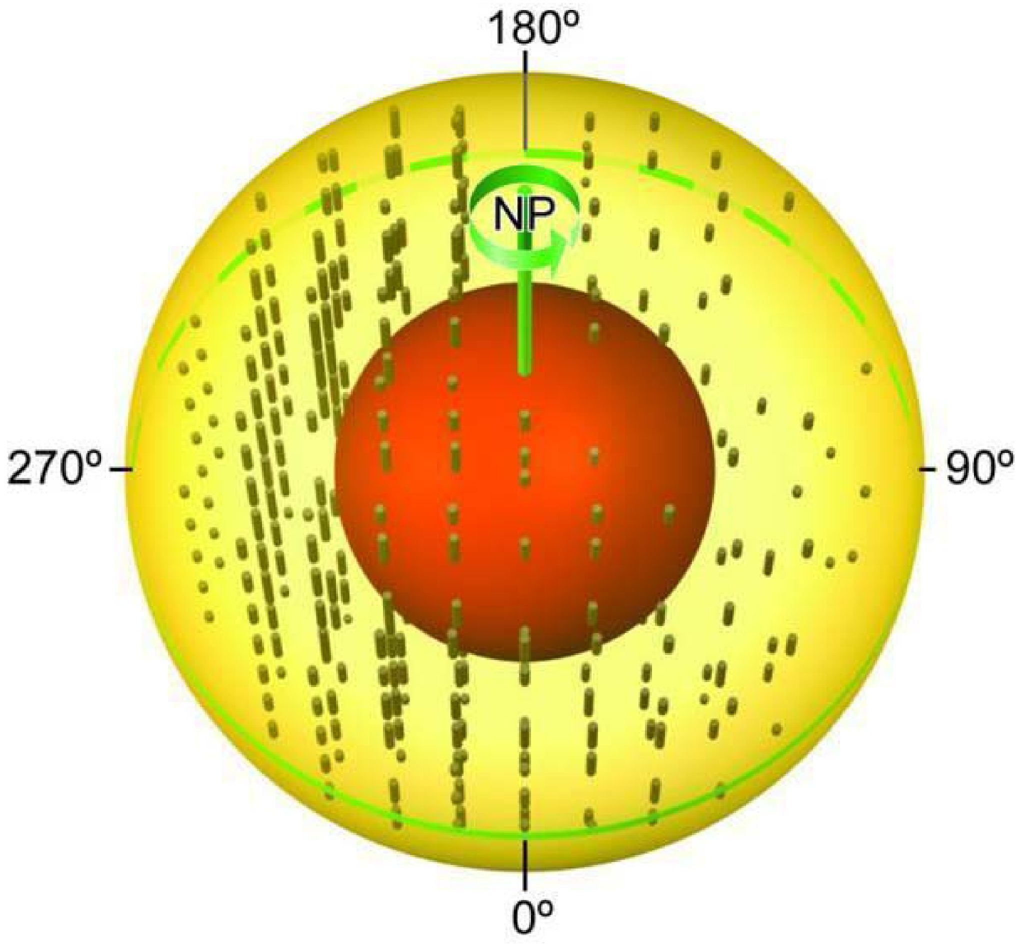


Alboussière *et al*, Nature 2010



Gubbins *et al*, Nature 2011

The Inner Core



Sun & Song 2008

- Layering with OIC and IIC
- Significant anisotropy
- Hemispherical variations in anisotropy for OIC
- Melting of inner core
- IIC distinct: either different phase or different crystalline alignment
- Preferred orientation of crystals over time leading to texture?

Finding out about the core: Computational Mineral Physics

- Seismology is the direct observation

- Gives elastic properties and their variations as a function of depth including lateral variations

- Calculate these properties on iron and iron alloys

- Match the seismology

What does CMP involve?

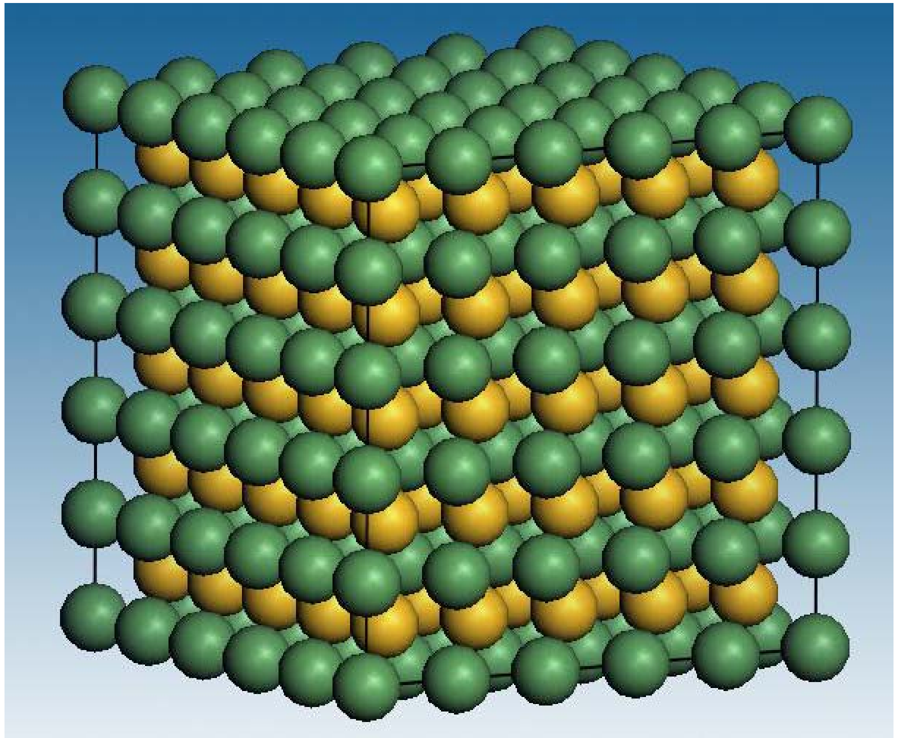
- Atomistic scale modelling of bonding in minerals and fluids
- The bonding is described by *quantum mechanics;* calculate how energy varies with structure.
- Solve Schrodinger’s equation, but problem with more than one electron

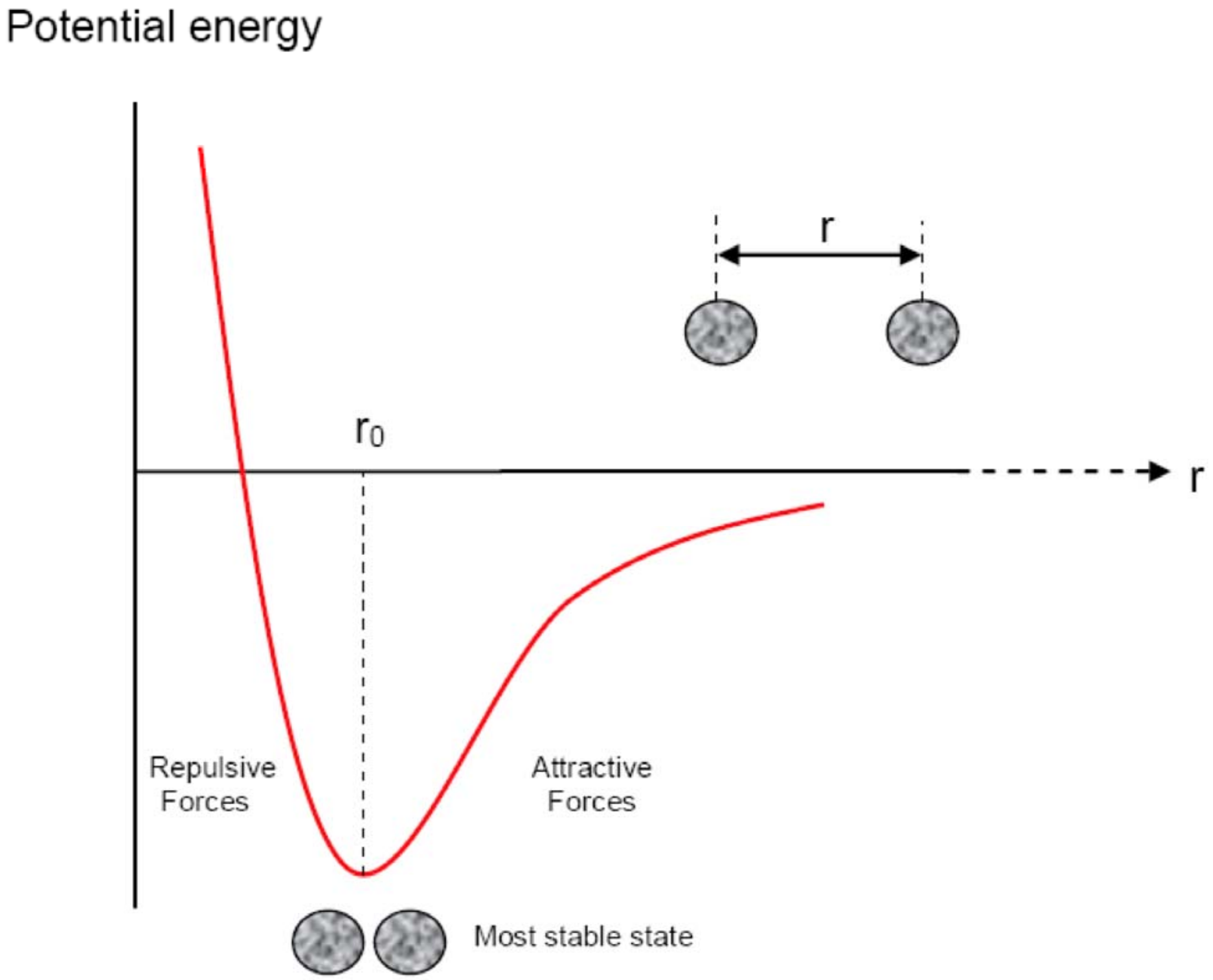
Ab initio techniques (or tricks)

- VASP code using DFT with PAW and GGA

  This is the trick that gets us past one electron

- Numerically solving Schrodinger's equation
- No parameterisation
- Can predict:
  - V(P), K, EoS
  - ω_i
  - C_{ij}, V_P, V_S
  - Free energies
  - Defects and diffusion
  - Viscosities and melting....

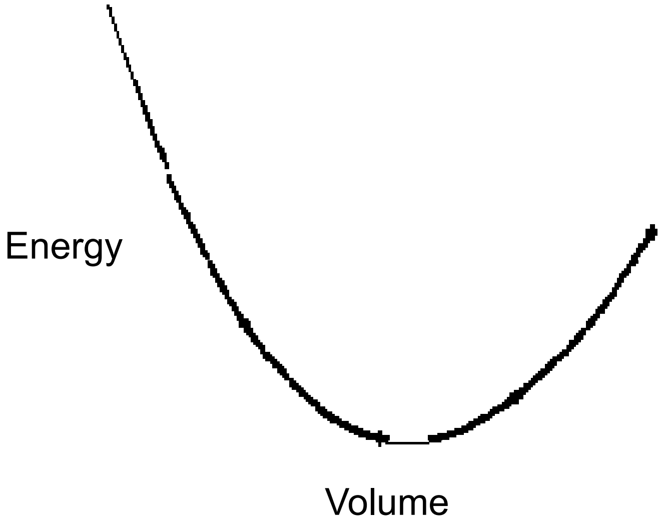


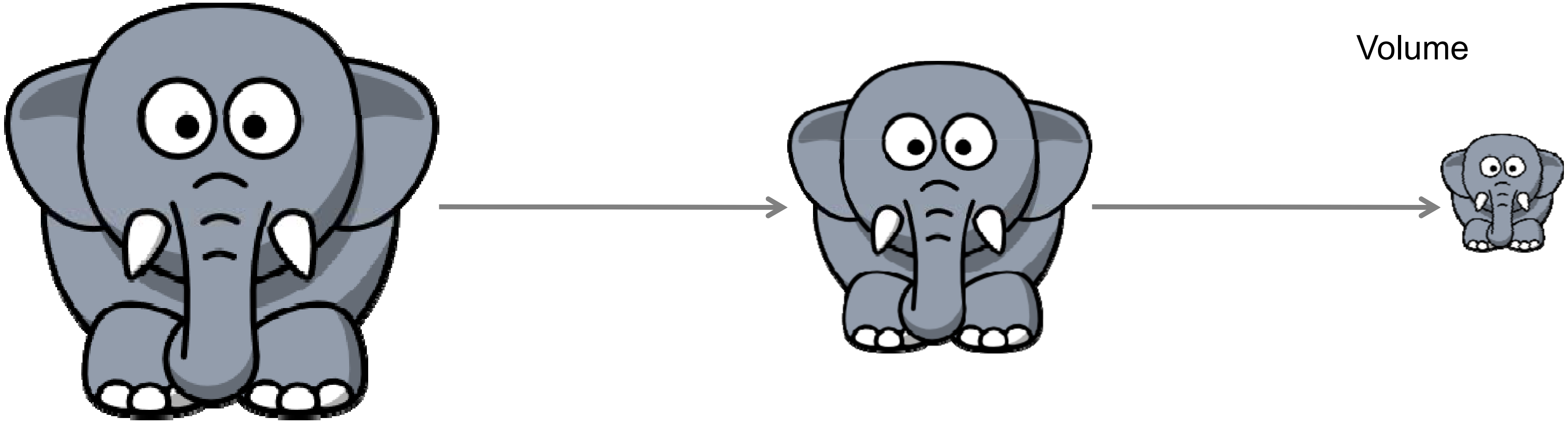


Potential energy as a function of atomic separation, r; the equilibrium bond length, r_0, corresponds to an energy minimum.

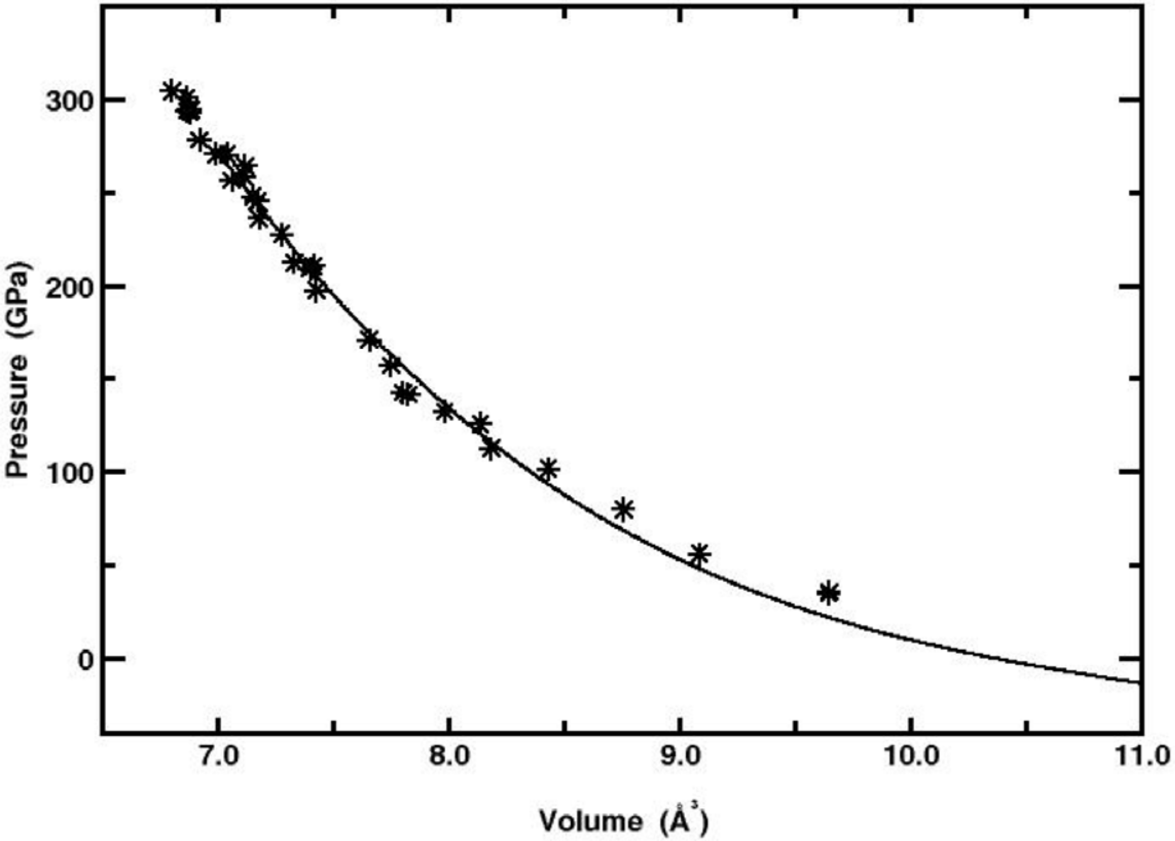
Simulation of pressure

- Choose V
- Vary atom positions and cell dimensions to produce minimum energy
- No residual forces on the atoms (dE/dx = 0)
- Calculate energy
- Change V and repeat
- Fit to an Equation of State





Equation of state for iron



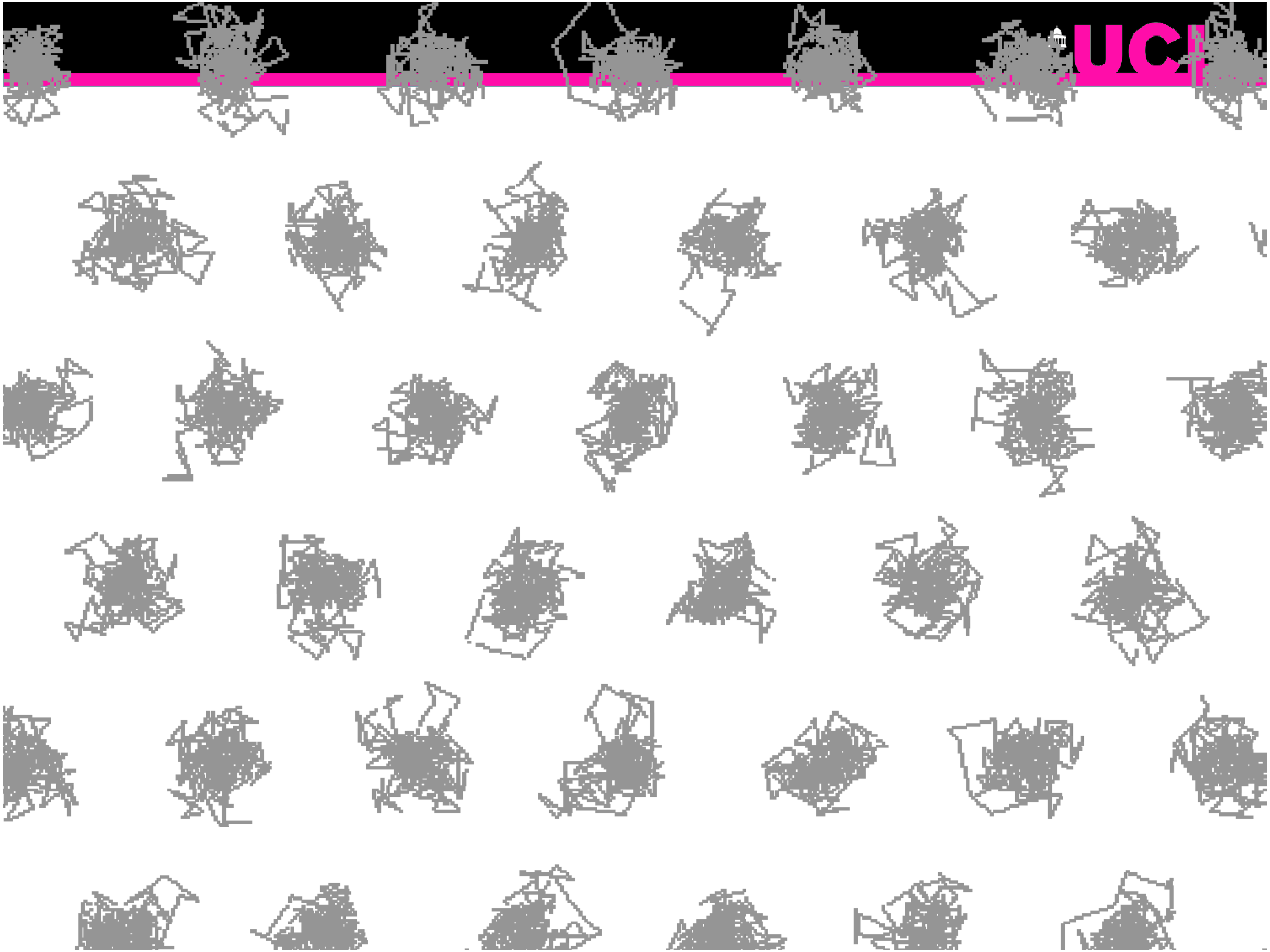
Vočadlo et al. Faraday Disc. 1997

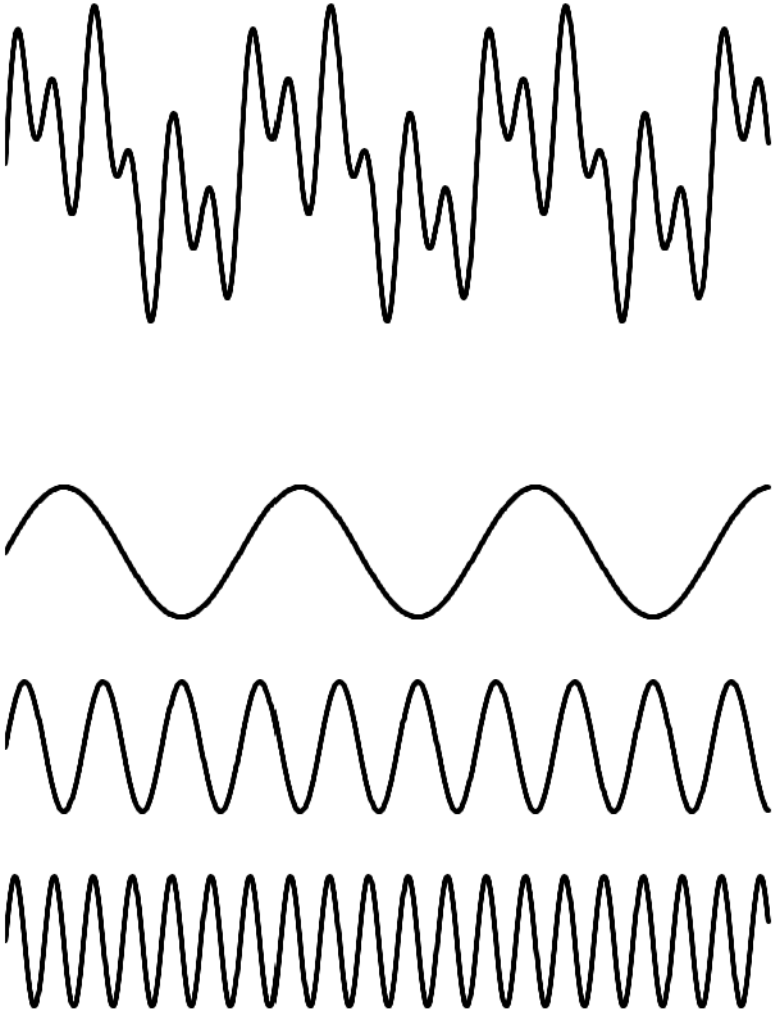
Simulation of Temperature

- Computationally more difficult that modelling P
- Two approaches:
  - Lattice Dynamics
  - Molecular Dynamics
- Very, very cpu expensive

Simulation of Temperature:

Lattice Dynamics





Any complex motion, such as the trace at the top, can be decomposed into a set of simple sine waves, each with a frequency, **ω_i** and wavelength, λ.

Thermodynamic Properties

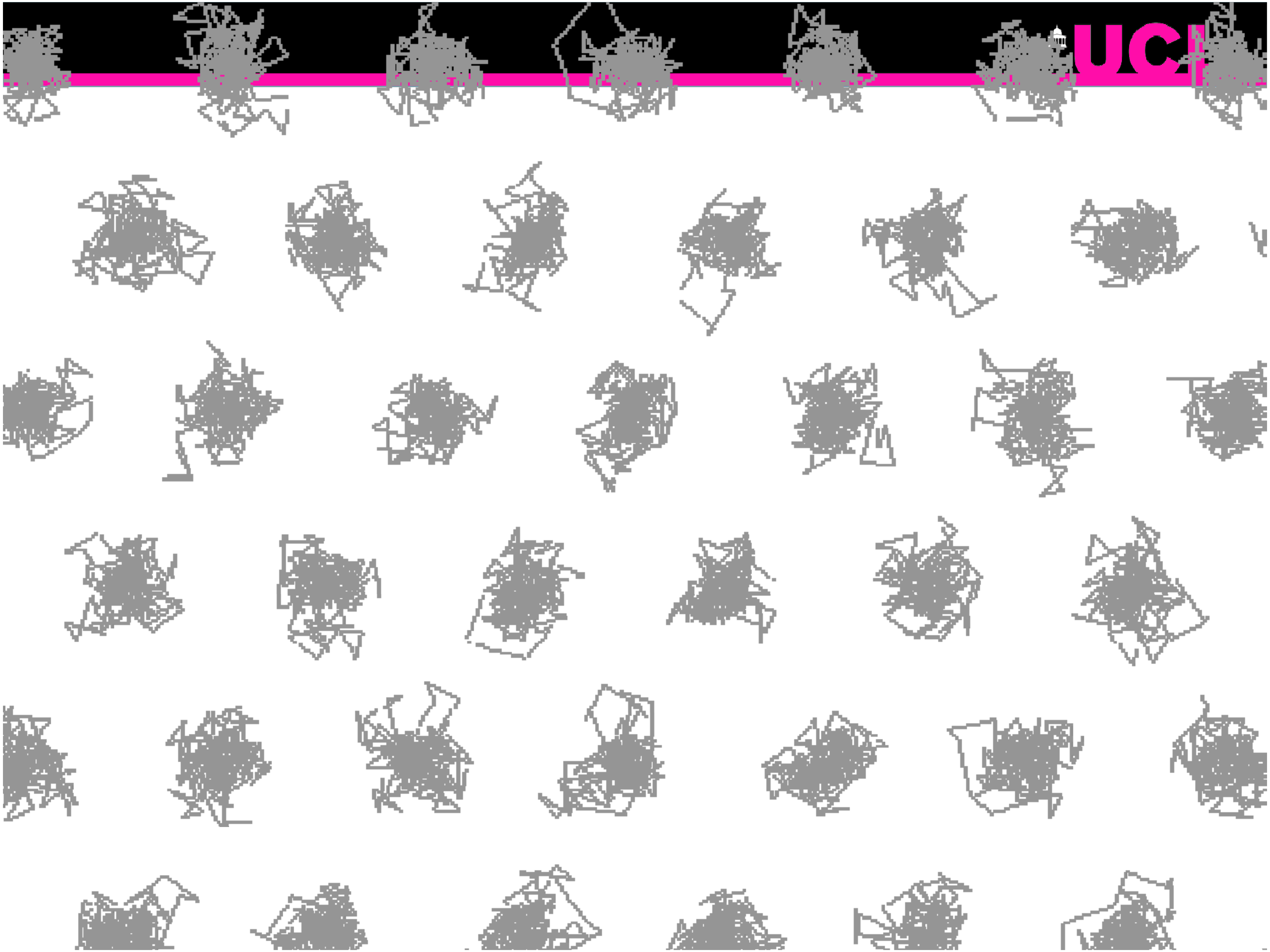
S, C, E, c_{ij}, etc. = $f(\boldsymbol{\omega_i})$

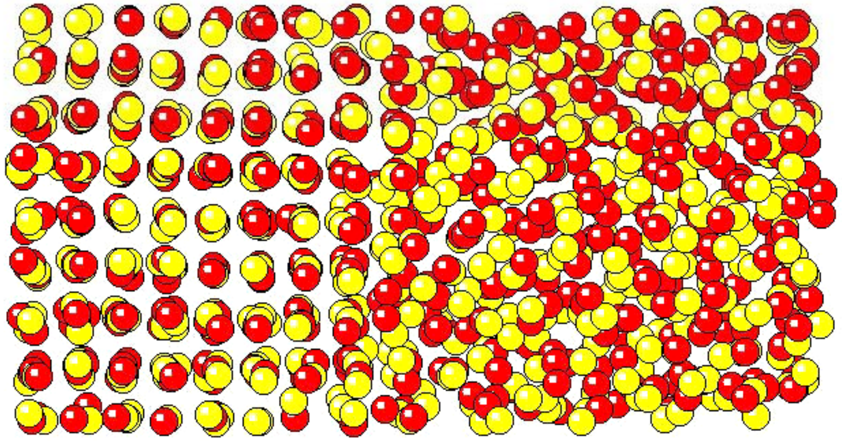
K, G, V_p, V_s = $f(c_{ij})$

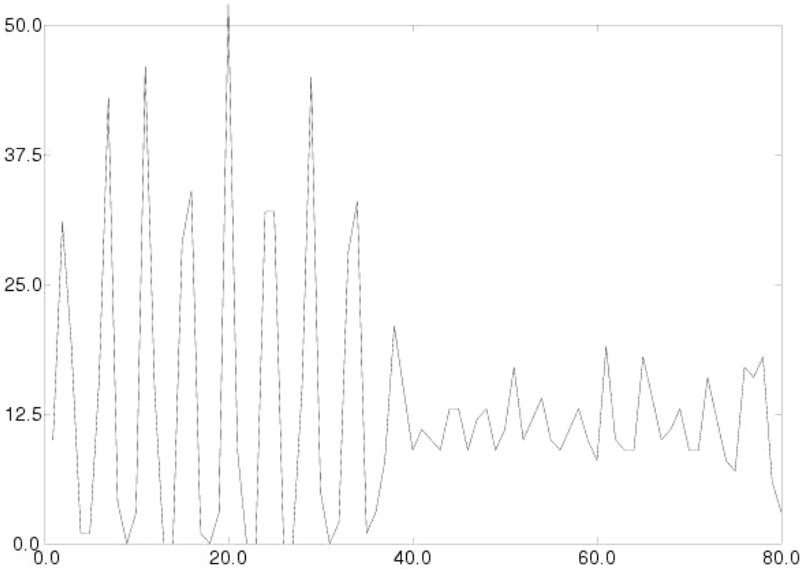
Free energy: $$F = k_B T \sum_i \frac{h\omega_i}{2k_B T} + \ln\left(1 - e^{-\frac{h\omega_i}{k_B T}}\right)$$

Simulation of Temperature:

Molecular Dynamics

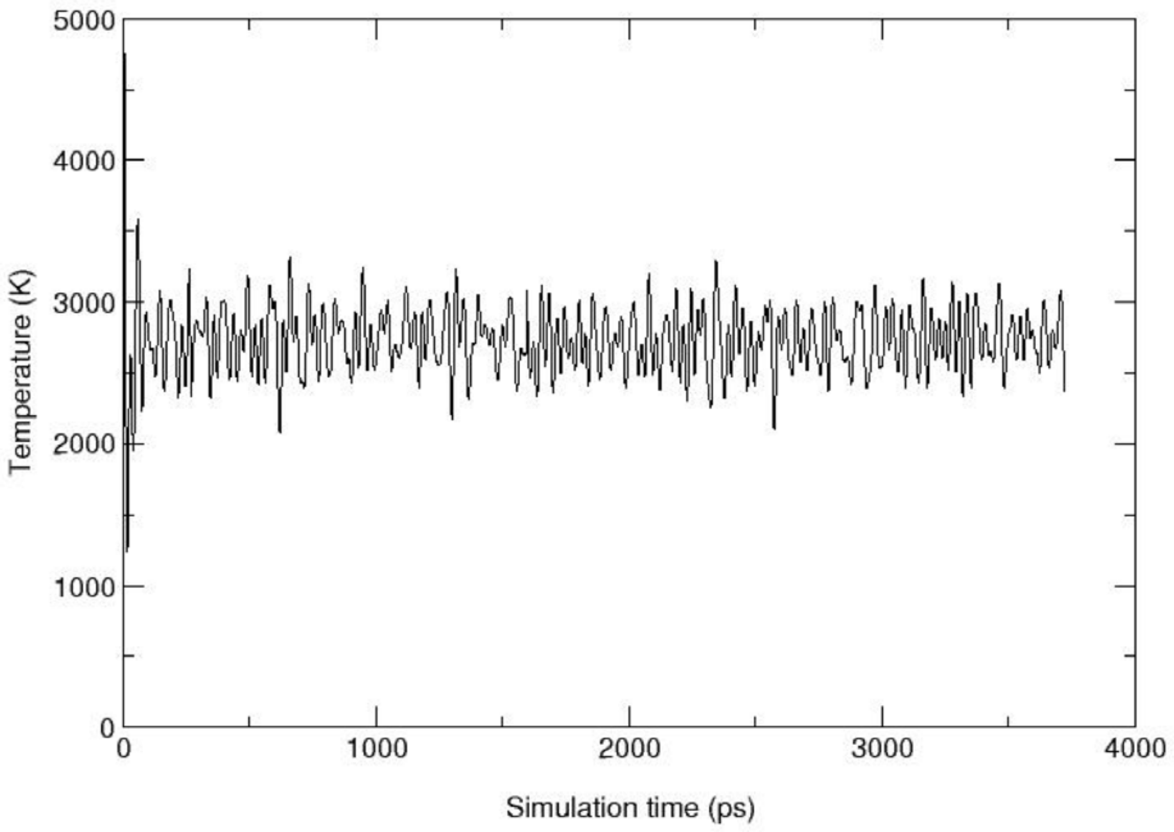






50.0
37.5
25.0
12.5
0.0
0.0
20.0
40.0
60.0
80.0

MD simulation output

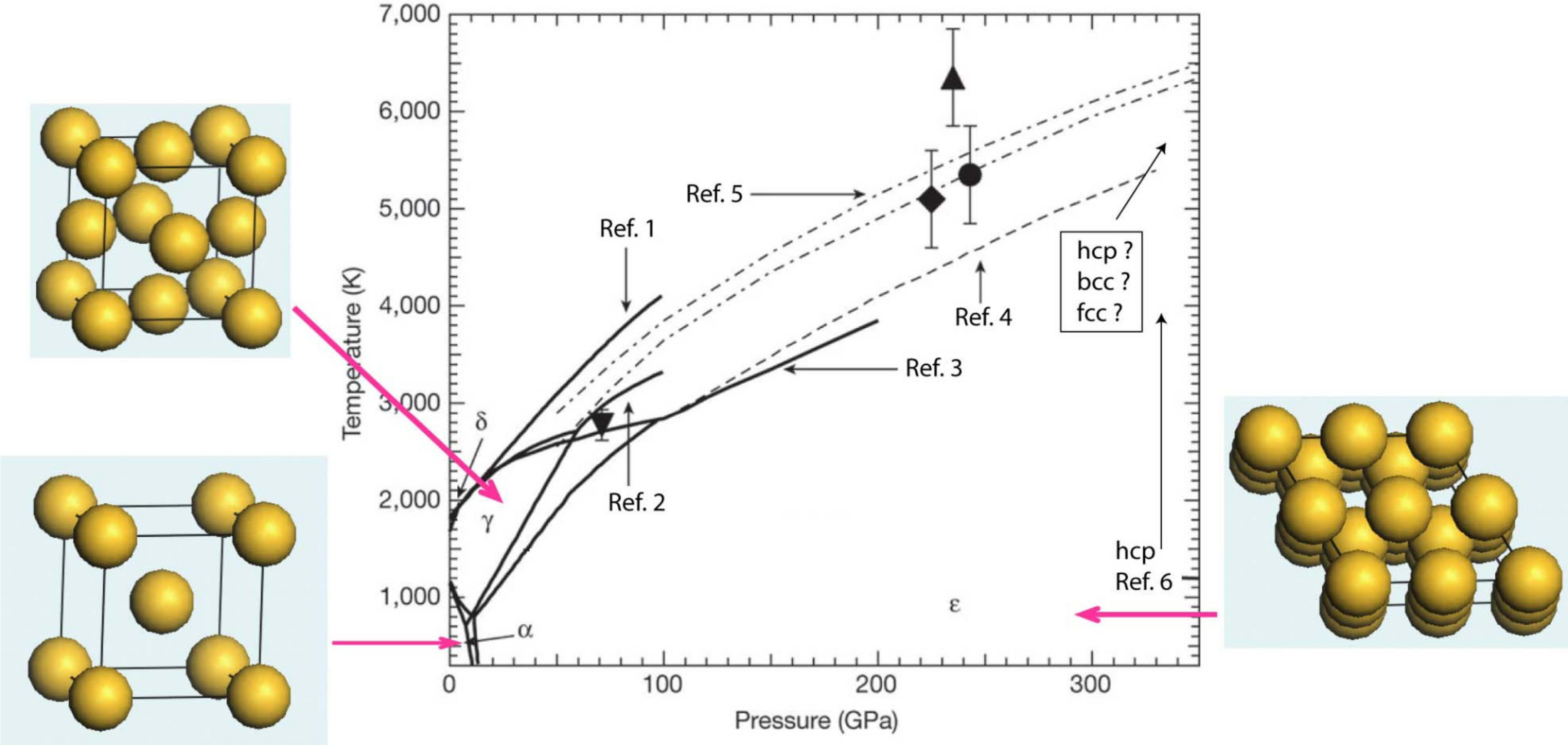


Ab initio molecular dynamics simulations of iron showing the time evolution of the temperature of the system calculated from the particle velocities. A similar trace is seen for many time-evolving properties (stress, energy…).

What’s the problem?

- What causes observed inner core complexity?
- Need to know what the core is made of
- Composition determined by stable phase(s) of Fe-X alloys
- First need to know stable phase of pure iron at core P&T
- Can we match V_P and V_S?
- Need to know effect of light elements
- Need to know the effect of nickel

Phase diagram of pure iron



Solid lines from DAC experiments; symbols from shock experiments; broken lines from first-principles calculations.

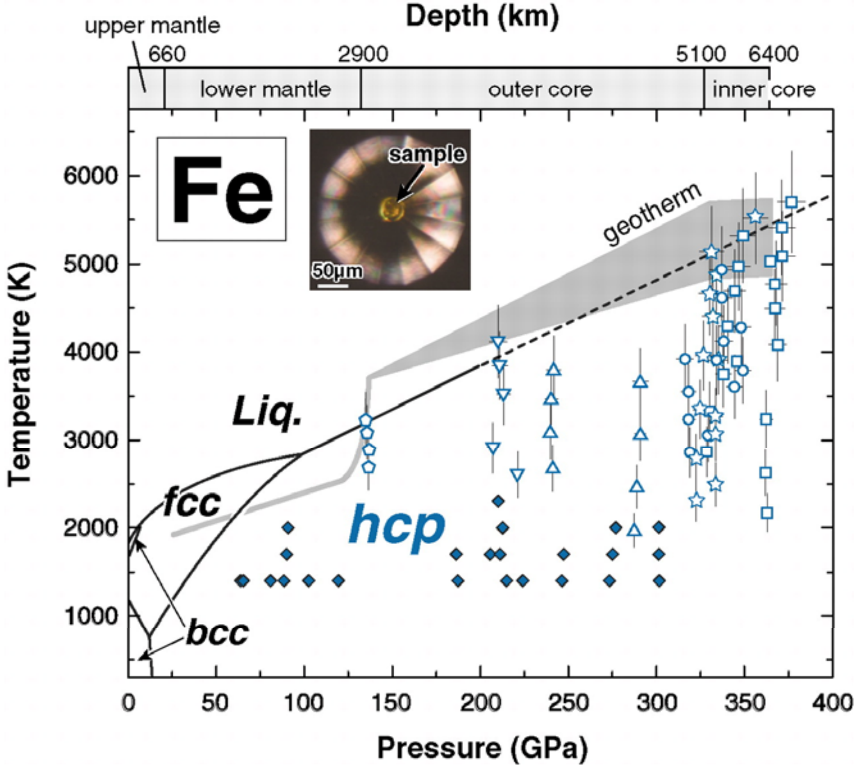
DAC data: Ref 1: Williams et al., 1987; Ref 2: Shen et al., 1998; Ref 3: Boehler, 1993. Shock data: triangle: Yoo et al., 1993; circles: Brown and McQueen, 1986; reverse triangle: Ahrens et al., 2002; diamond: Nguyen and Holmes, 2004. First principles calculations; Ref 4: Laio et al., 2000; Ref 5: Alfè et al., 2002; Ref 6: Vočadlo et al., 2000, 2003. Adapted from Nguyen and Holmes, 2004.

Free energy from molecular dynamics

- ρ = 13,155 kgm^{-3},T = 5500 K

- F_{hcp}(eV) F_{bcc}(eV) F_{fcc}(eV)
  -10.668 -10.633 -10.654

$$\Delta F_{bcc\text{-}hcp} = 35 \text{ meV}$$
$$\Delta F_{fcc\text{-}hcp} = 14 \text{ meV}$$



So for a inner core of pure Fe, stable phase is hcp

now confirmed experimentally by Tateno et al. (2010)

BUT there are light elements to consider

Vočadlo et al. 2003, 200

Can we match V_P and V_S? Both $f(C_{ij})$

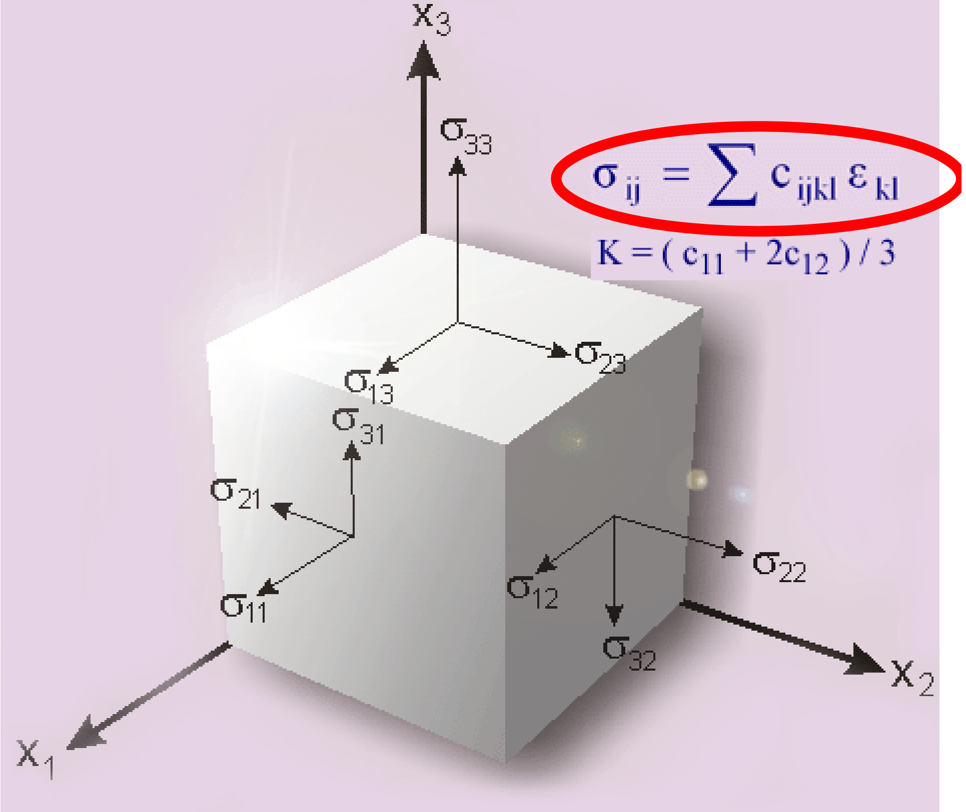
Seismic velocities of pure iron from elastic constants

- Only C_{11}, C_{12} and C_{44}
- Deformation matrix:

$$\begin{pmatrix} 1+\delta & \delta/2 & 0 \\ \delta/2 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

- For hcp need two strain matrices in order to get C_{11}, C_{12} C_{13}, C_{33} and C_{44}

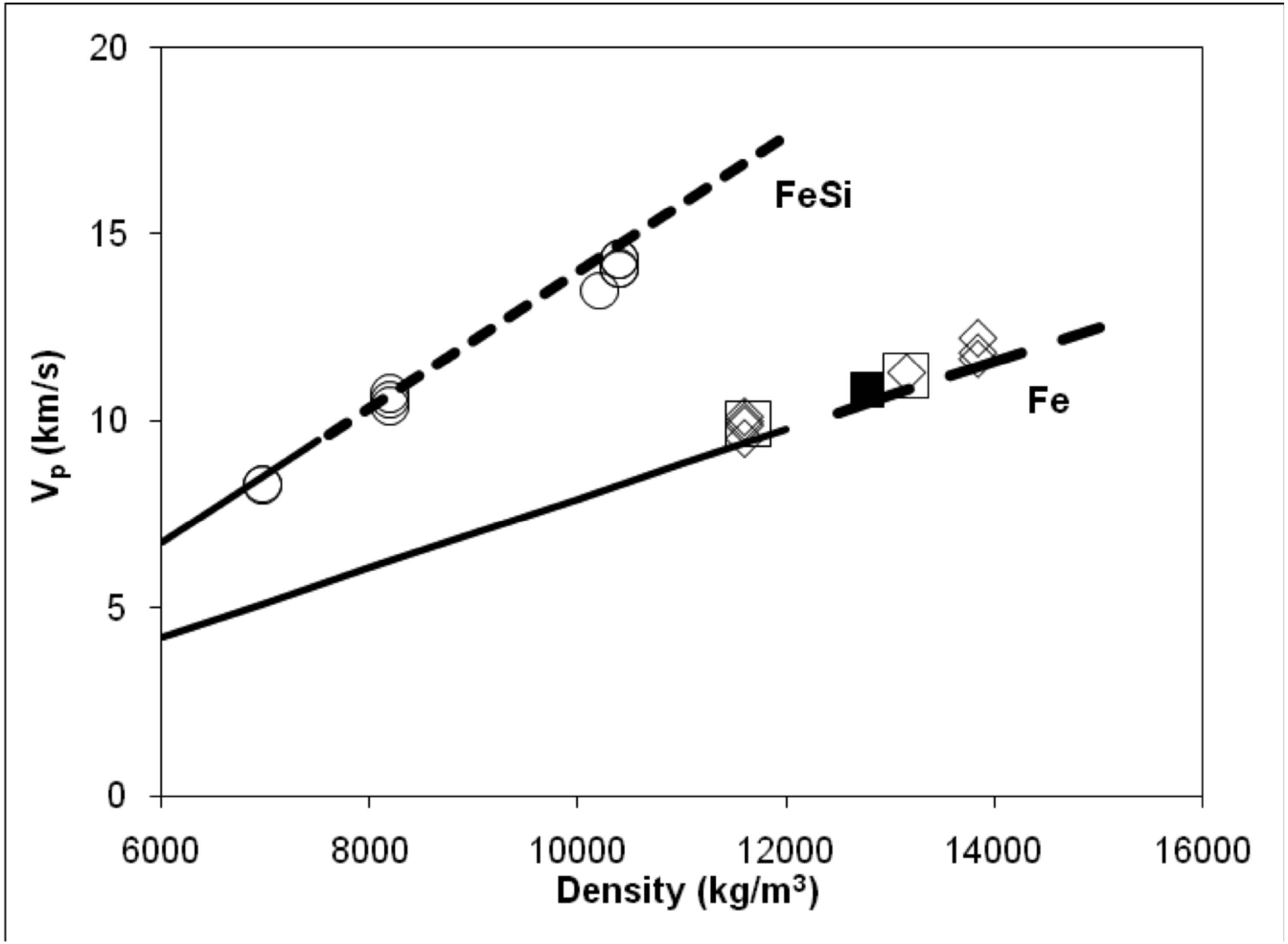
All done at core P&T



$$\sigma_{ij} = \sum c_{ijkl}\,\varepsilon_{kl}$$

$$K = (c_{11} + 2c_{12})/3$$

Must remember to match "real" data



Can we match V_P and V_S?

Not yet……

- AIMD elasticity calculations show high V_S for all phases (Vočadlo 2007, Vočadlo et al., 2008)

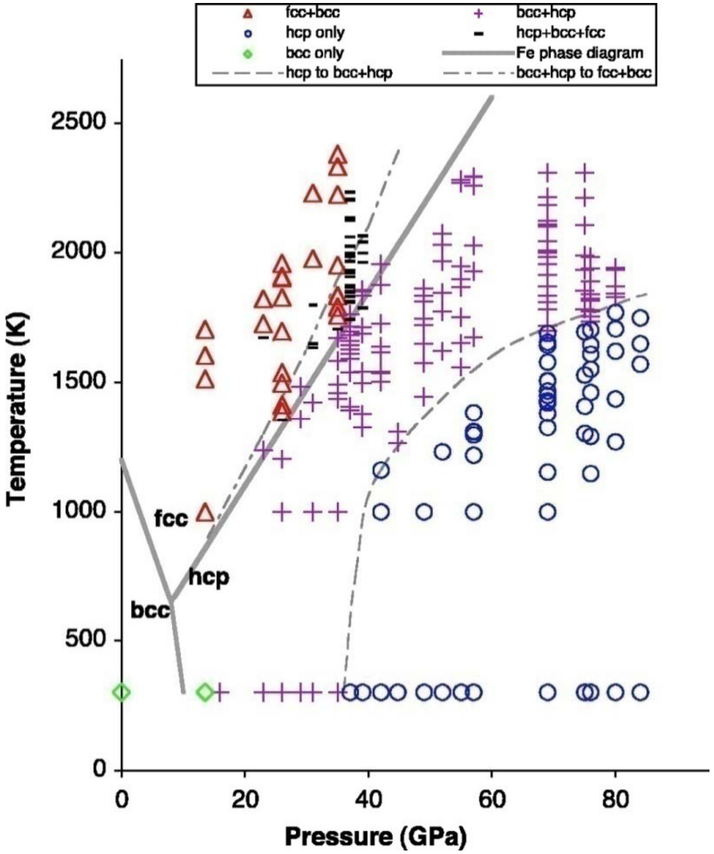
	ρ (kgm^{-3})	**T (K)**	**V_P (kms^{-1})**	**V_S (kms^{-1})**
hcp-Fe	13155	5500	11.14	4.01
bcc-Fe	13155	5500	11.29	4.11
fcc-Fe	13155	5500	11.64	4.64

- Incompatible with seismology: V_S (PREM) = 3.5-3.67 kms^{-1}
- Calculated V_S > seismology by 10-30 %
- Needs a lot of melt in the IC to account for difference in V_S:

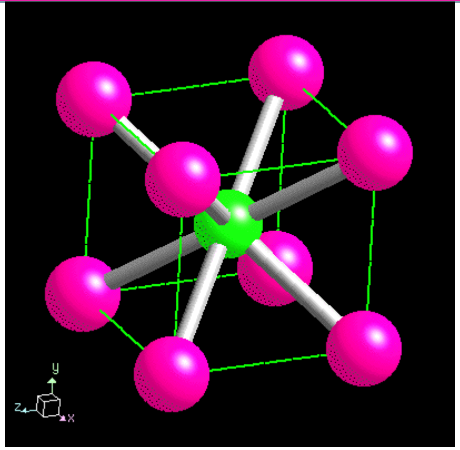
%: $>8_{bcc}$ $>12_{hcp}$ $>25_{fcc}$

(% melt estimate from Hashin–Shtrikman bound for effective μ of 2-phase media)

The effect of light elements



LH-DAC of Fe with 7.9 wt. % Si.
Lin et al. (2002)



- Cold calculations predict transition to the CsCl-FeSi at ~13 GPa (Vočadlo et al. 1999)

- CsCl-FeX iso-structural with bcc

- CsCl-FeSi (Dobson et al., 2002)
- CsCl-FeS (Sata et al., 2008)
- CsCl-FeO (Ozawa et al., 2011)

- **At zero K**, 330 GPa, few atm. % Si, S, O, C stabilises bcc-Fe (Côté et al. 2008)

Problem is even worse…..

	ρ (kgm^{-3})	**T (K)**	**V_P (kms^{-1})**	**V_S (kms^{-1})**
hcp-Fe	13155	5500	11.14	4.01
bcc-Fe	13155	5500	11.29	4.11
fcc-Fe	13155	5500	11.64	4.64
cubic-FeSi	10212	5500	13.53	6.26
cubic-FeS	10353	5500	12.02	4.43
fcc-Fe_3S	13155	5500	11.97	4.55

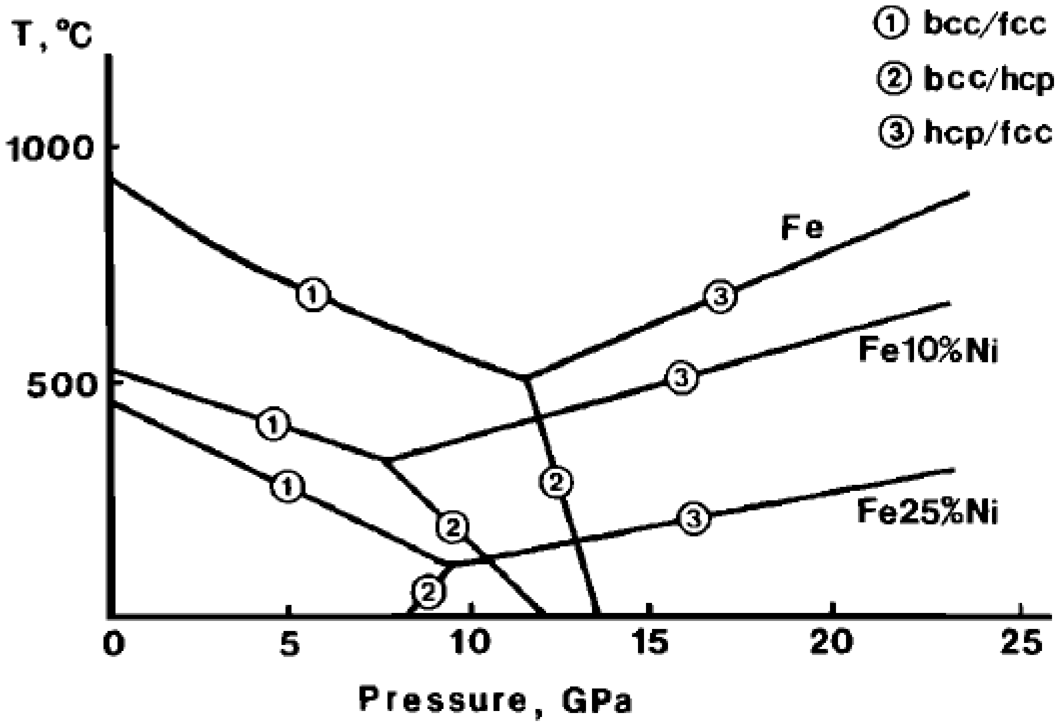
- Incompatible with seismology: V_S (PREM) = 3.5-3.67 kms^{-1}
- Calculated V_S > seismology by 10-50+ %
- Needs a lot of melt in the IC to account for difference in V_S:

%: $>8_{bcc}$ $>12_{hcp}$ $>25_{fcc}$

Possible explanations include

- partial melt
- anelasticity
- lateral density inhomogenities
- aggregates and defects in iron
- composition effects

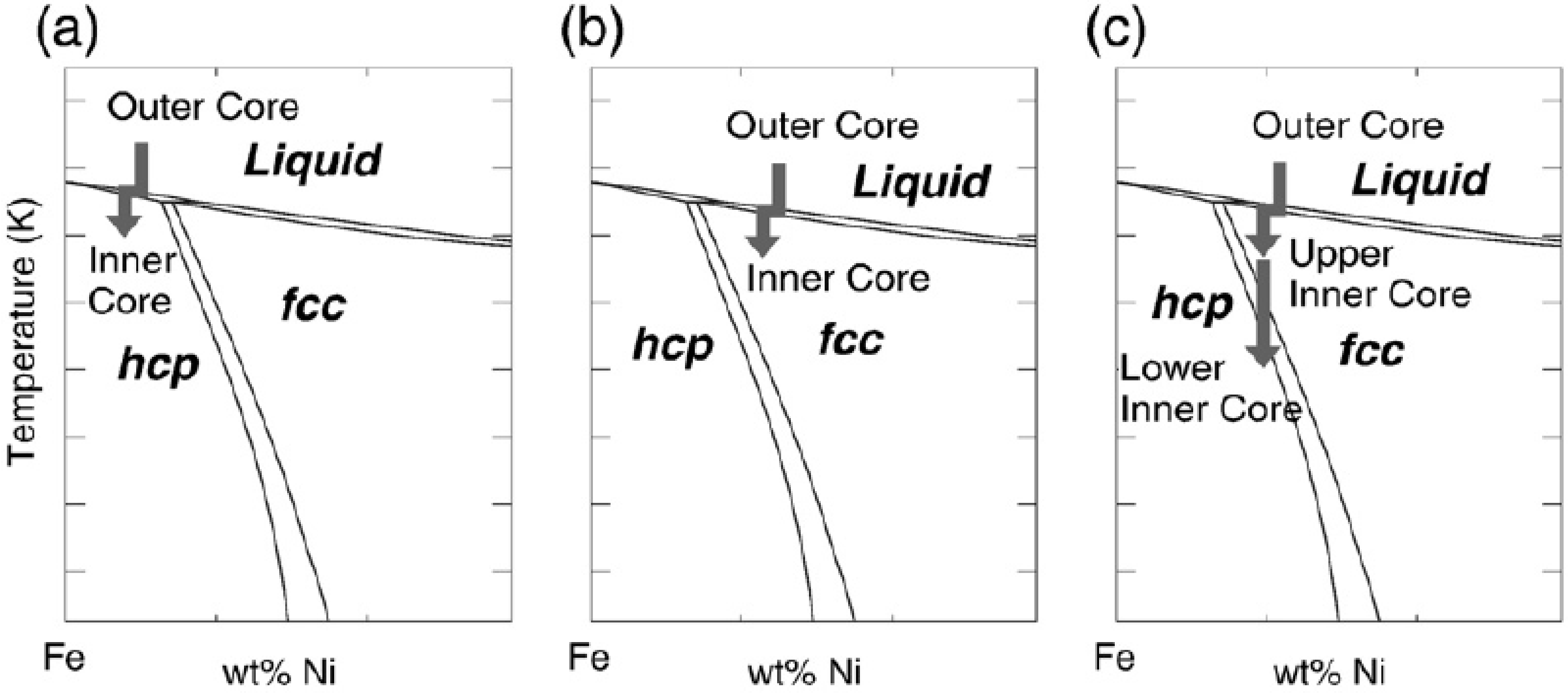
But.... Ni works the opposite way to light elements



DAC experiments of Huang et al. (1988); qualitatively in agreement with calculations of Vočadlo et al., 2006

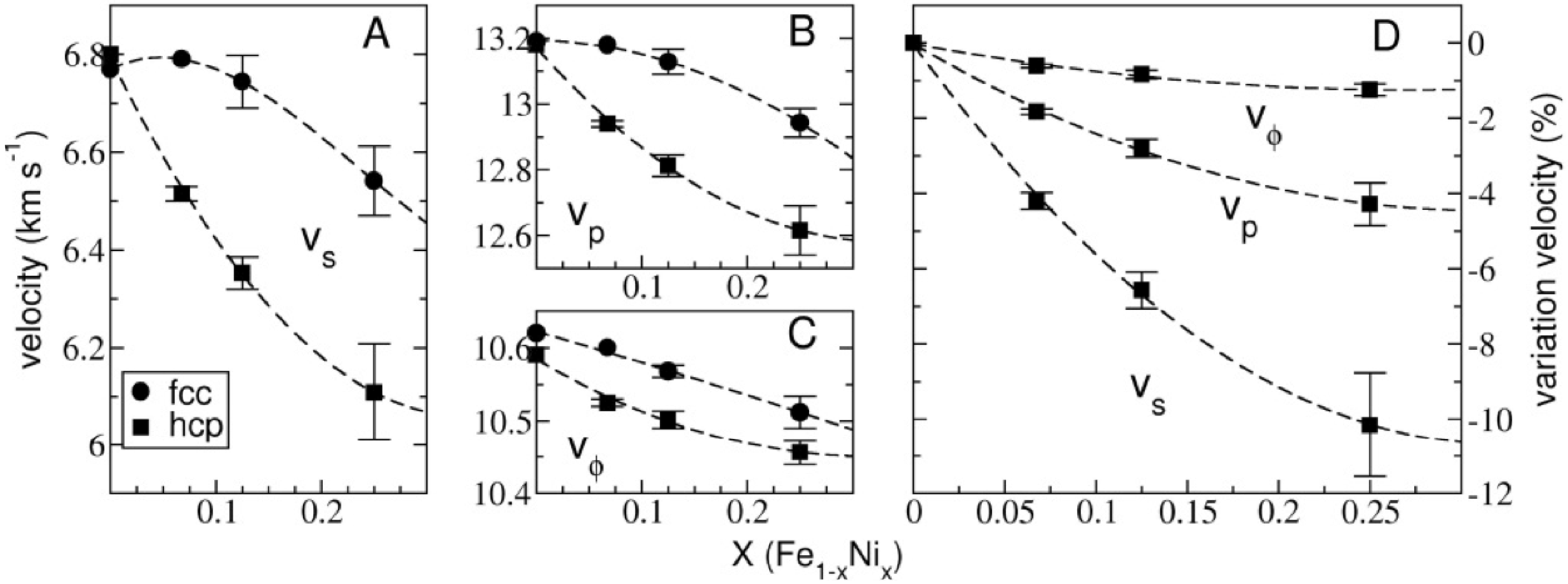
LHDAC at ~300 GPa and ~2000 K

Y. Kuwayama et al. / Earth and Planetary Science Letters 273 (2008) 379–385



- Triple point is “possibly” located at ~10-20 wt% Ni
- Crystallising phase depends on % Ni present
- Could have early crystallising of fcc phase, then hcp on cooling (3rd figure)
- Could explain layering in inner core
- However, we calculate ~40% Ni required before fcc transition

Ab initio V_P, V_S on hcp-Fe-Ni



NB These are cold calculations done at 360 GPa… hot calculations in progress!

Summary: a very simple explanation

- Observed V_S are at least 10% lower than those of Fe and Fe-light element alloys at core conditions
- Do not need assorted complicated explanations
- Ni has an unexpectedly large effect on the velocities, particularly V_S, of the hexagonal close-packed (hcp) phase.
- Depending on the concentration of Ni in the core, our results show that the observed velocities in the Earth's inner core are consistent with an Fe-Ni alloy in the hcp structure, with a low concentration of light-element.

Birch (1952): High Pressure Language

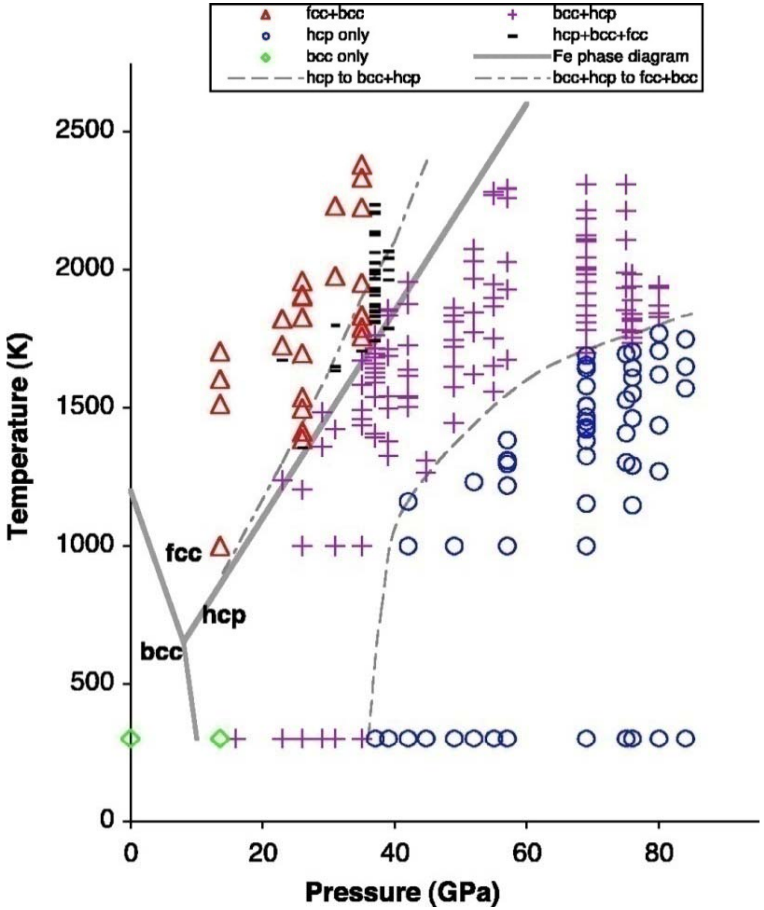
High pressure form:	***Ordinary meaning:***
pure iron	*uncertain mixture of all the elements*

Core solutions? Or more problems….

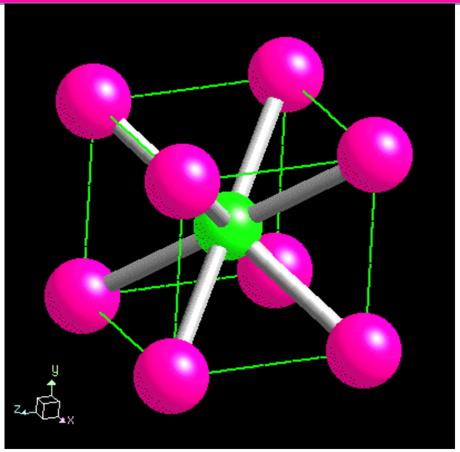
- Seismology giving much more detailed (interesting) structure of the core
- Inner core phase *if it was pure iron* would be hcp
- The presence of light elements and nickel changes everything
- But the free energy difference is always very very small
- Likely to be an "*uncertain mixture of all the elements*"

- The high V_S for all phases is incompatible with seismology
- Needs a lot of melt in the inner core (%: $>8_{bcc}$ $>12_{hcp}$ $>25_{fcc}$)
- Anisotropy can be accounted for by fcc and hcp, not bcc!

What about light elements?



LH-DAC of Fe with 7.9 wt. % Si.
Lin et al. (2002)



- Cold calculations predict transition to the CsCl-FeSi at ~13 GPa (Vočadlo et al. 1999)

- CsCl-FeX iso-structural with bcc

- CsCl-FeSi (Dobson et al., 2002)
- CsCl-FeS Sata et al., 2008

- **At zero K**, 330 GPa, few atm. % Si, S, O, C stabilises bcc-Fe (Côté et al. 2008)

Free energy from lattice dynamics

$$F = k_B T \sum_i \frac{h\omega_i}{2k_B T} + \ln\left(1 - e^{-\frac{h\omega_i}{k_B T}}\right)$$

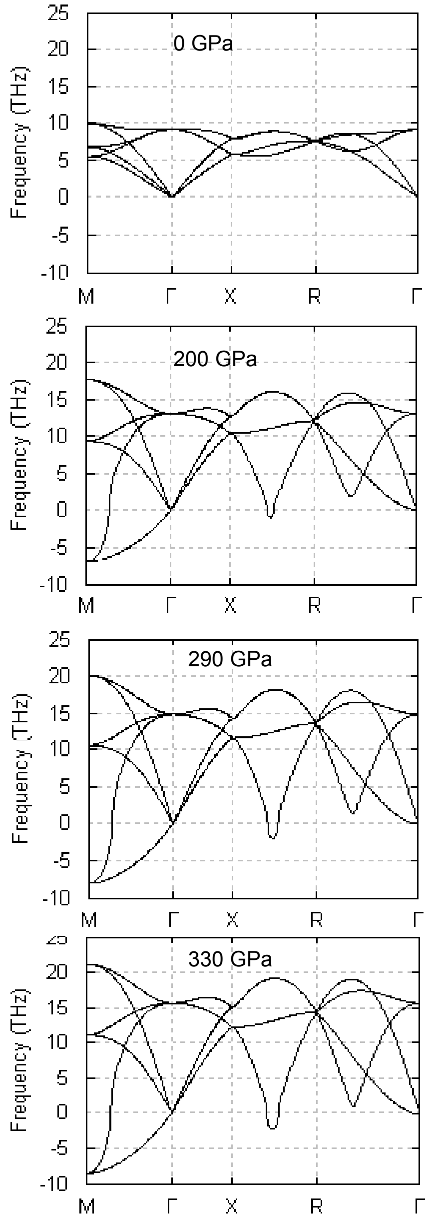
$$G = F + PV$$

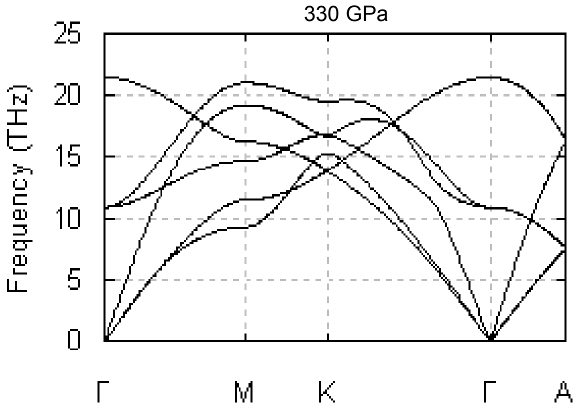
- ω_i from phonon calculations
- Calculations zero K; T added at this stage

Phonon spectra of iron

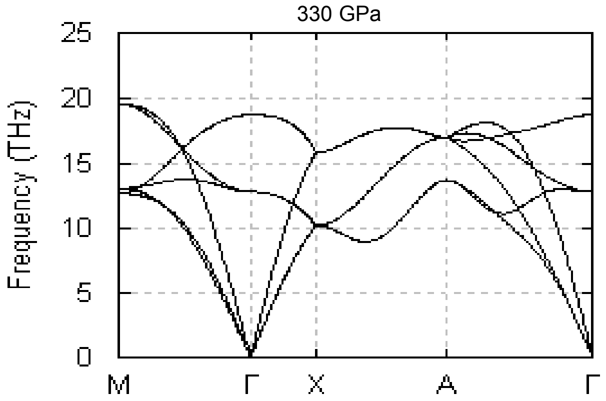
- Phonon dispersion as f(P)
- bcc becomes unstable at core P
- hcp and fcc vibrationally stable
- hcp more stable than fcc
- Cannot compare F_{bcc} with F_{hcp} or F_{fcc}

bcc





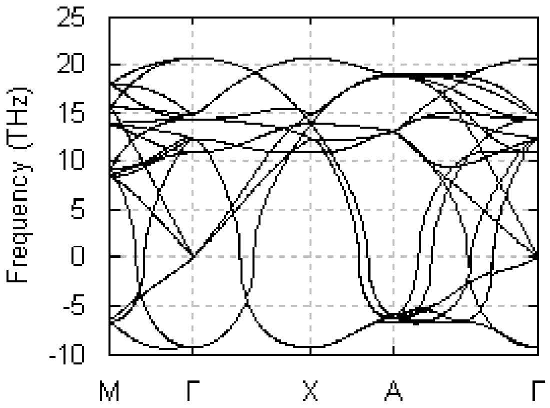
hcp-Fe



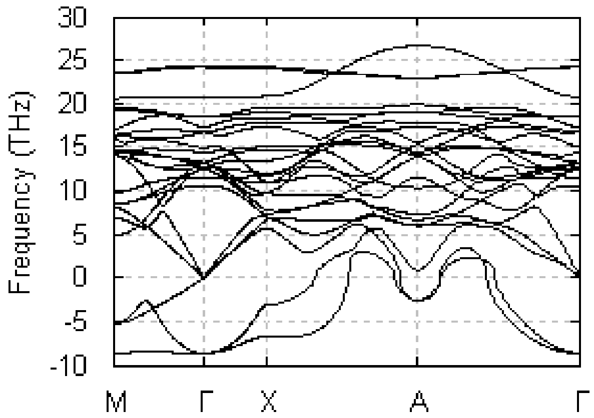
fcc-Fe

Phonon dispersion for *bcc-Fe* with Si

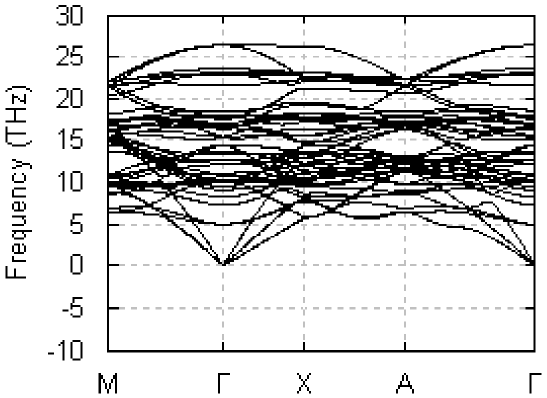
P = 330 GPa



Pure Fe



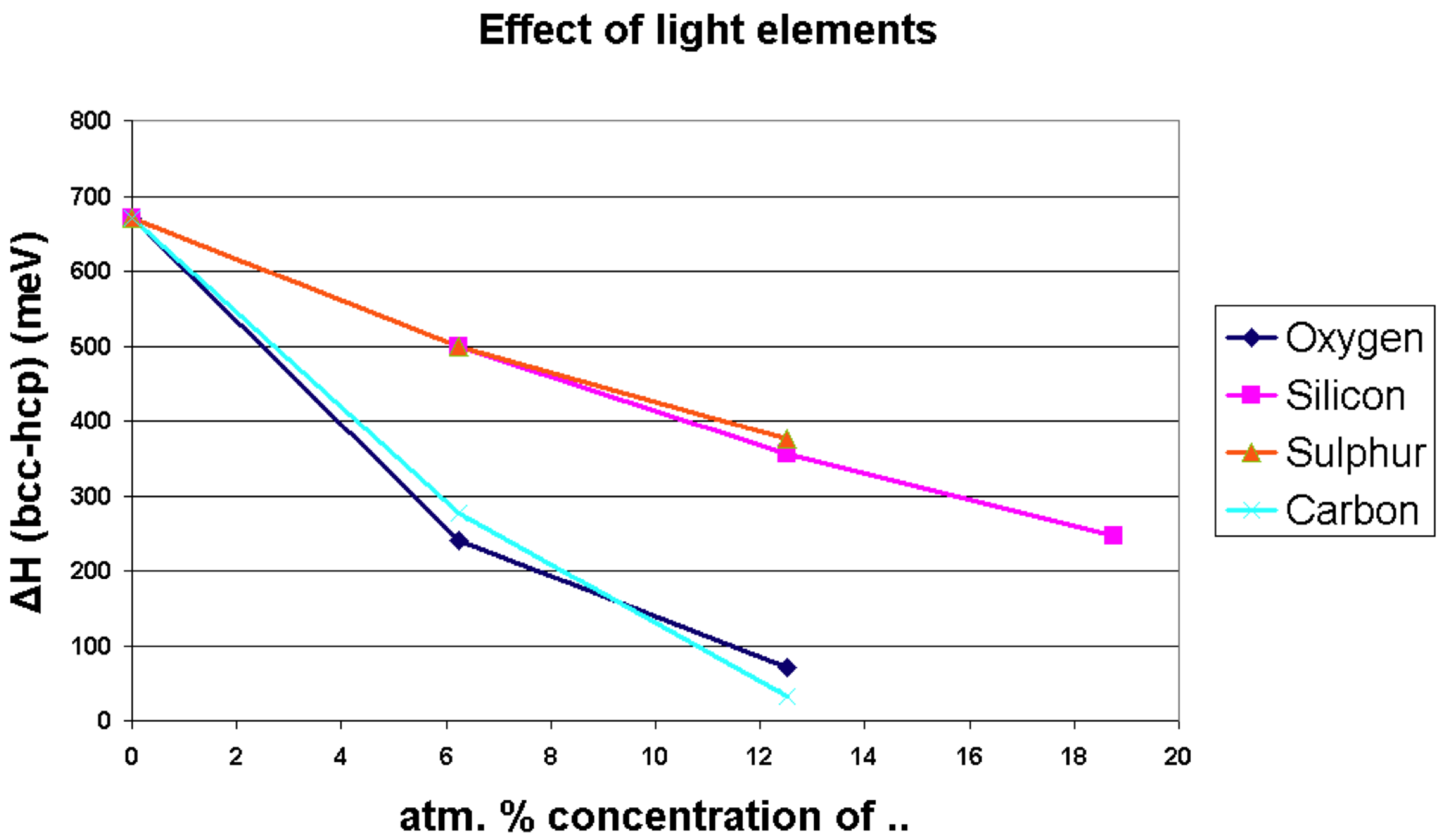
6.7 wt.% Si



10.4 wt.% Si

Silicon stabilises the *bcc-Fe* phase at high pressure

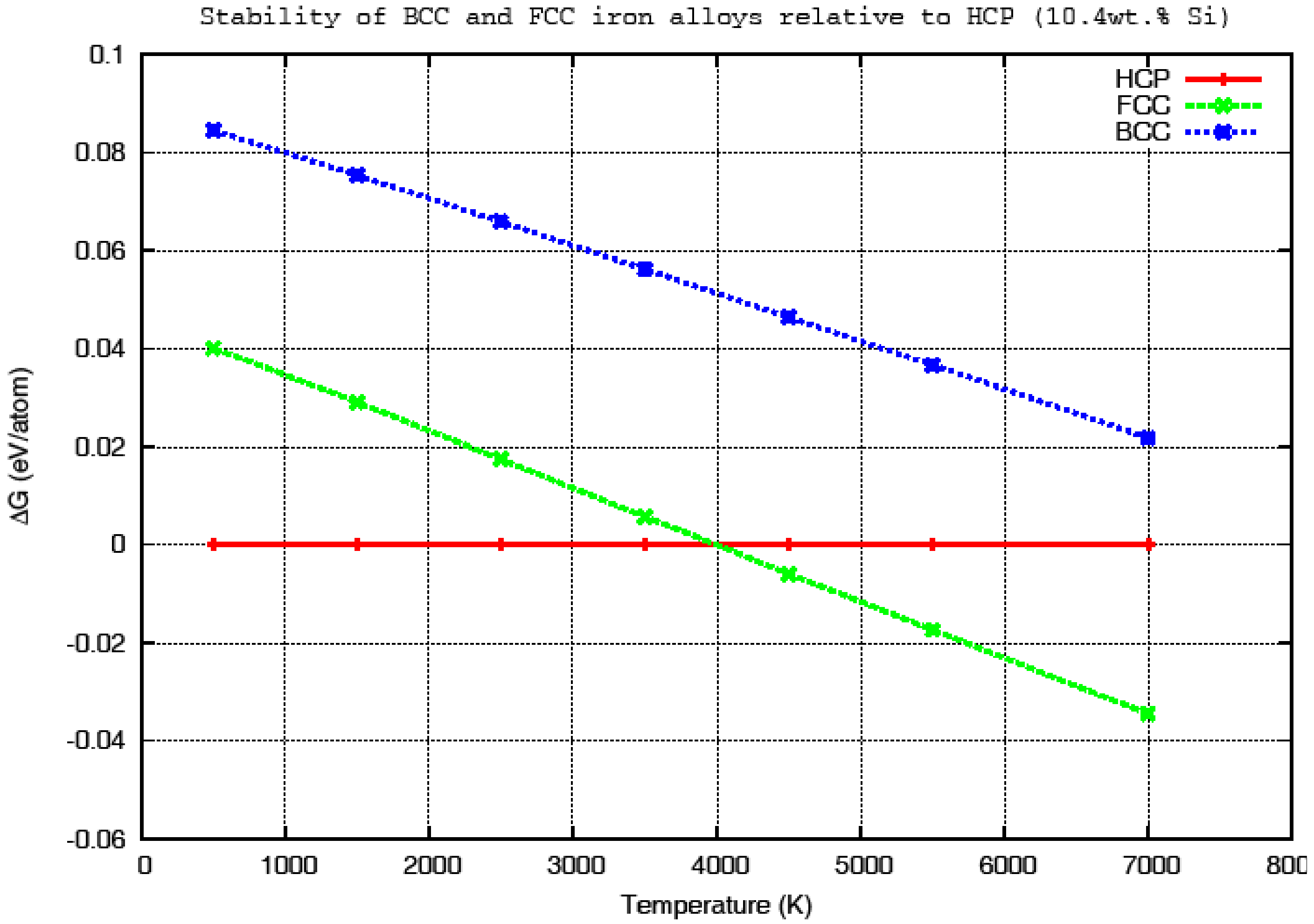
The Core: the only way out is in…….



NB Zero K

Cöté et al. (2008)

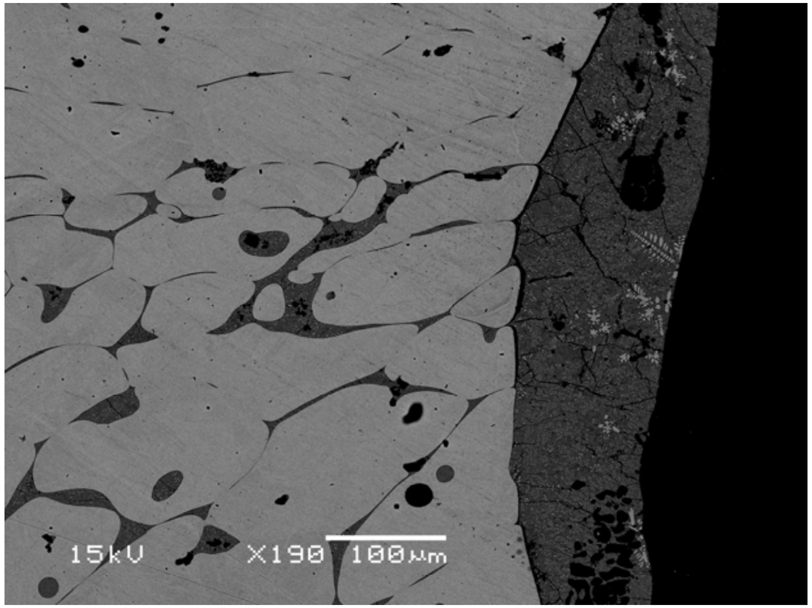
Stability of Fe with 10.4 wt.% Si at 330 GPa



Dihedral angle and planetary segregation

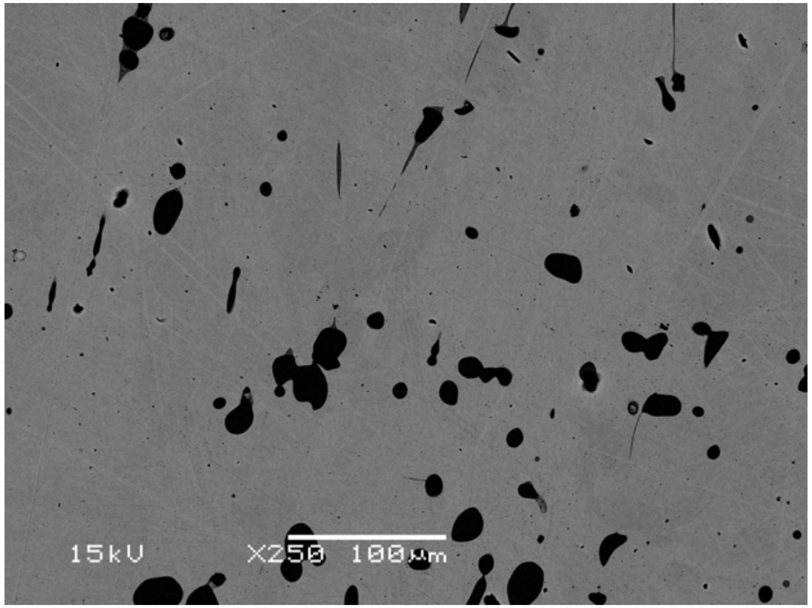
High T, 4 GPa

Fe-S in Fe



Low γ (~27^o) results in segregation

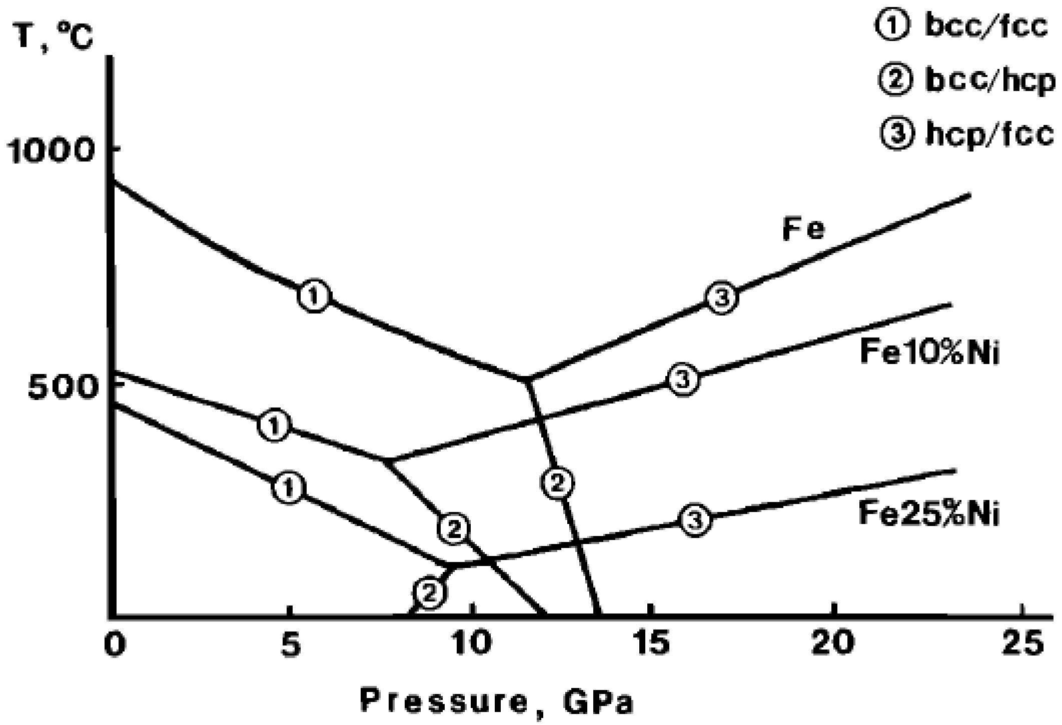
Fe-O in Fe



High γ (138^o) results in isolation

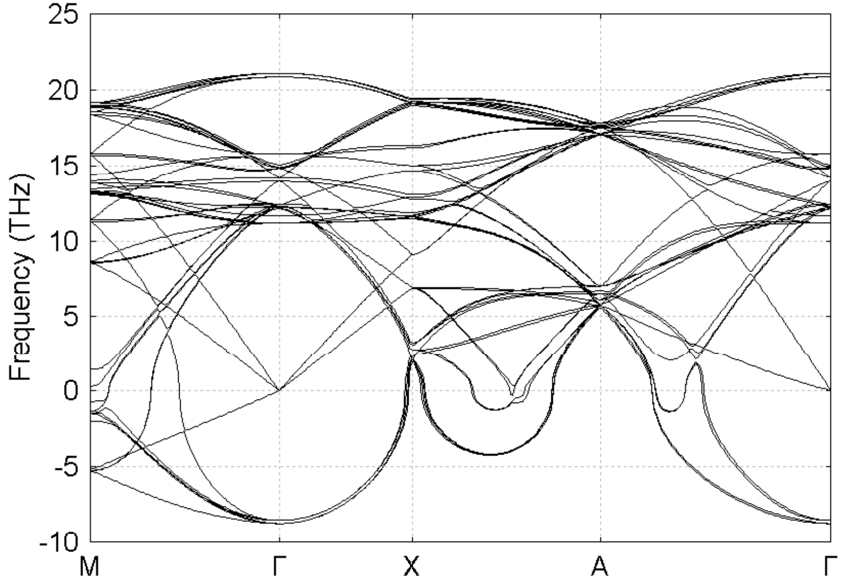
Immiscible system = high γ; low γ = miscible system
What happens at planetary core P? What about Si, C....??
Implications for crystallisation dynamics of terrestrial cores (Fe-Si-O alloys)

But.... Ni works the other way....

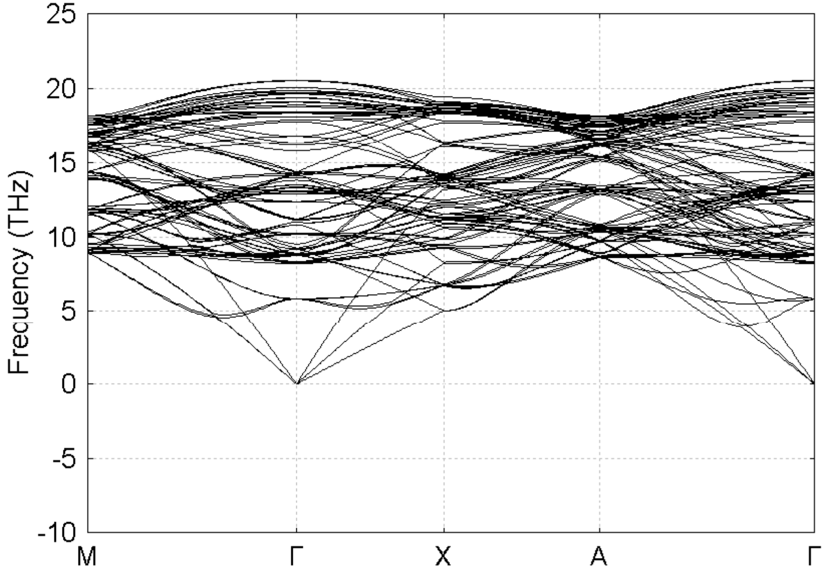


DAC experiments of Huang et al. (1988); qualitatively in agreement with calculations of Vočadlo et al., 2006

What about nickel?
Phonon dispersion for *bcc-Fe* with Ni
P = 330 GPa



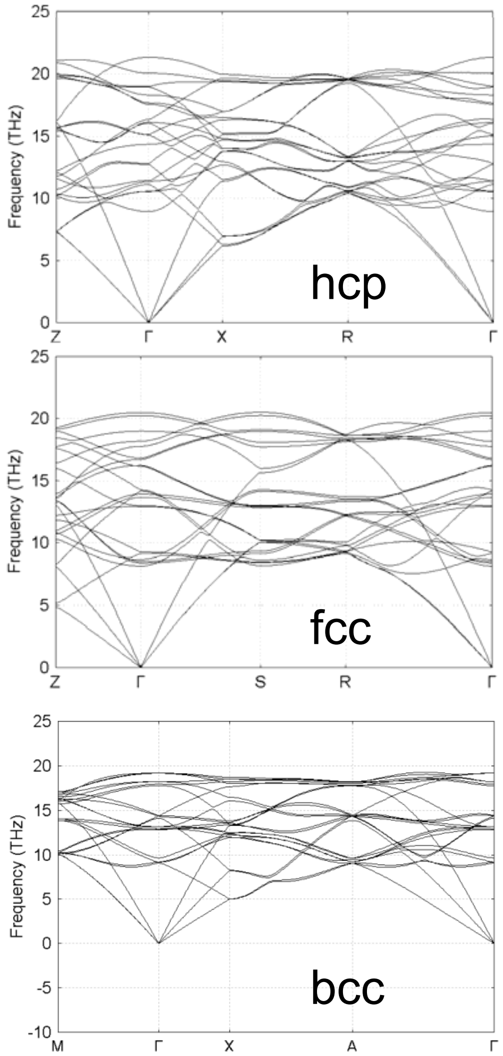
6.25 atm. %

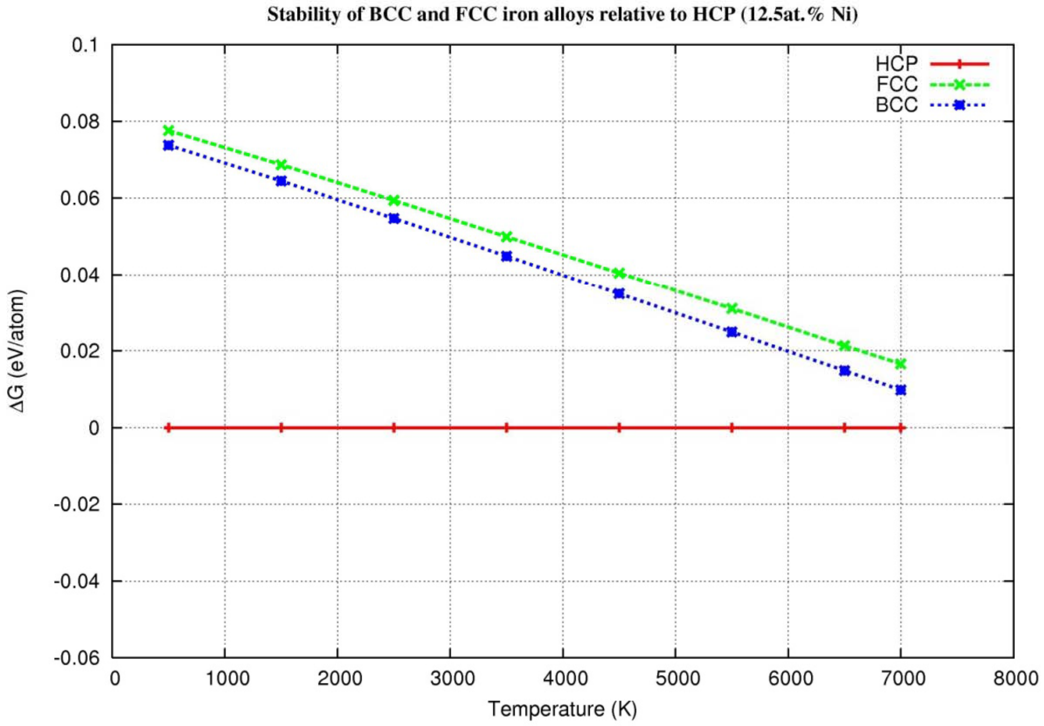


9.375 atm. %

Phonon dispersion for *hcp- and fcc-Fe* with Ni

P = 330 GPa, 12.5 atm % Ni





ΔG ~ 20-30 meV at 5500 K

These are not big numbers!

Stable phase of Fe in the IC according to UCL:

It’s hcp…. (1999)

No, it’s bcc... (2003)

Oh, ok, it’s hcp..... (2008)

No it’s fcc...... (2009)

It’s an uncertain mixture of all the elements…. (2011)

Is it because of anelasticity…..

The reduction in V_S due to shear wave attenuation is given by:

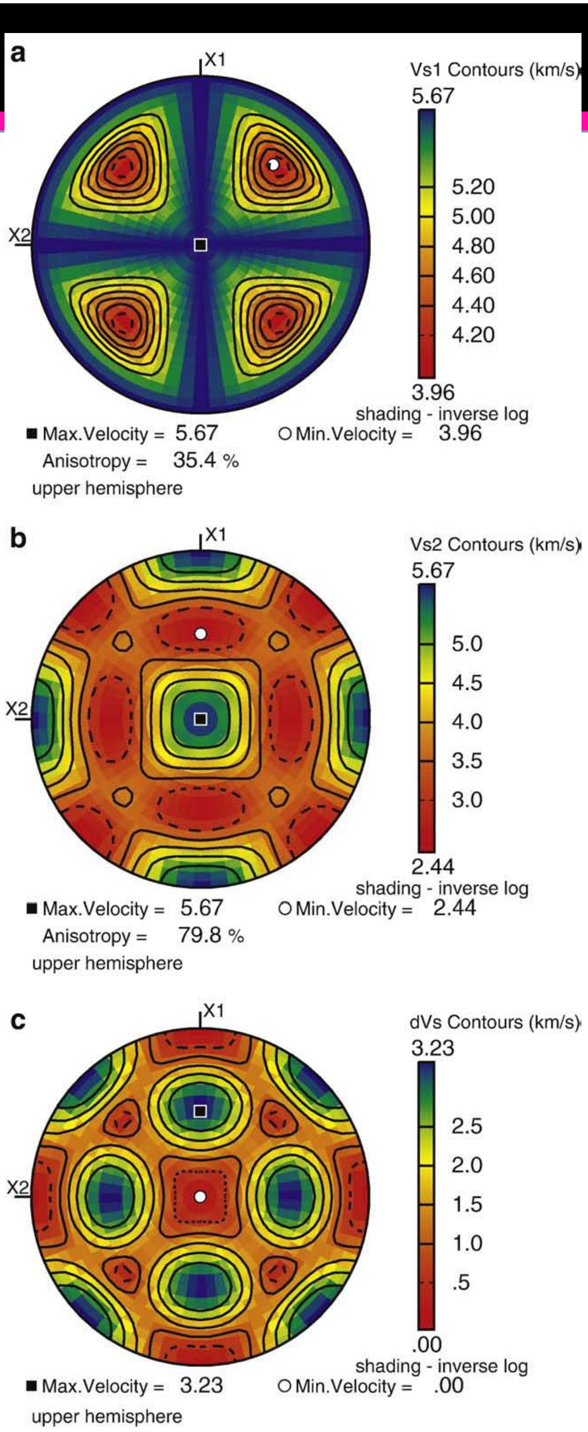
$$V(\omega,T)=V_0(T)\left(1-\frac{1}{2}\cot\left(\frac{\pi\alpha}{2}\right)Q^{-1}(\omega,T)\right)$$

For the inner core:

Quality factor, Q = 100 *(Resovsky et al., 2005)*

freq dep of Q, α = 0.2-0.4 *(Jackson et al., 2000)*

This results in a decrease in the shear velocity of only 0.5-1.5%, nowhere near the >8% difference between the seismological observations and the calculated materials properties.

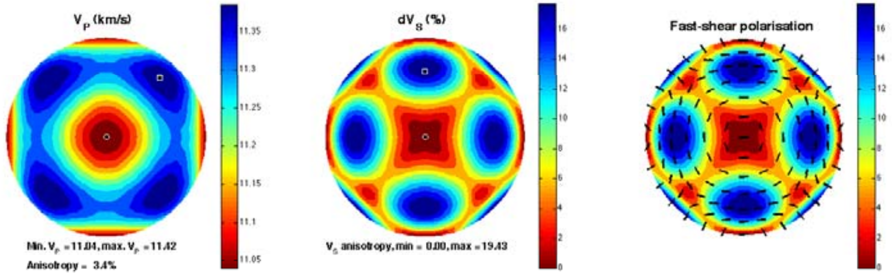


Single crystal S-wave velocities in fcc-Fe as a function of propagation direction:

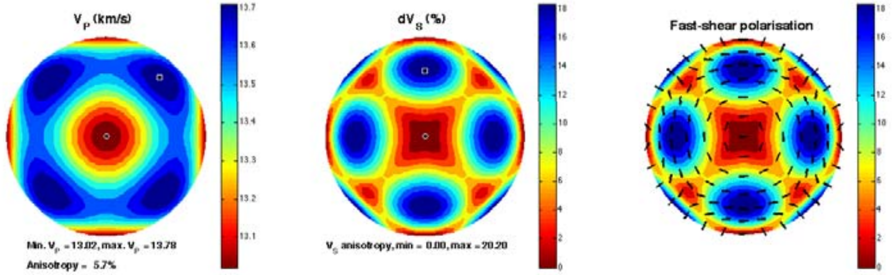
a) V_{S1}
b) V_{S2}
c) dV_S

- Anisotropy strikingly large....
- Much larger than bcc- and hcp-Fe

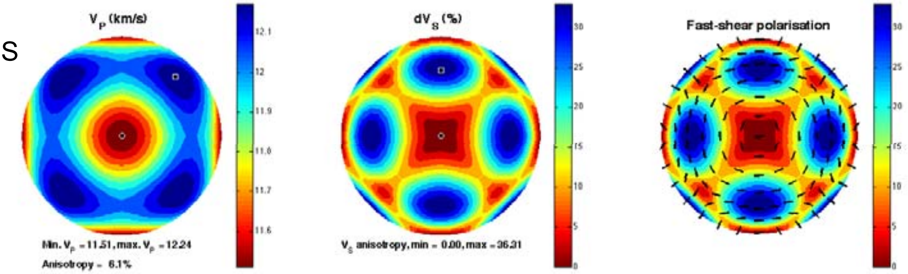
bcc-Fe



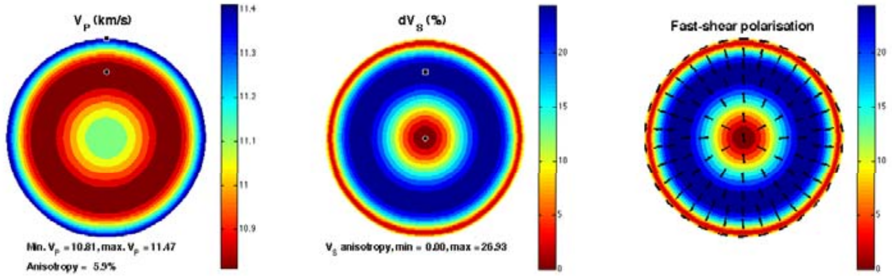
FeSi

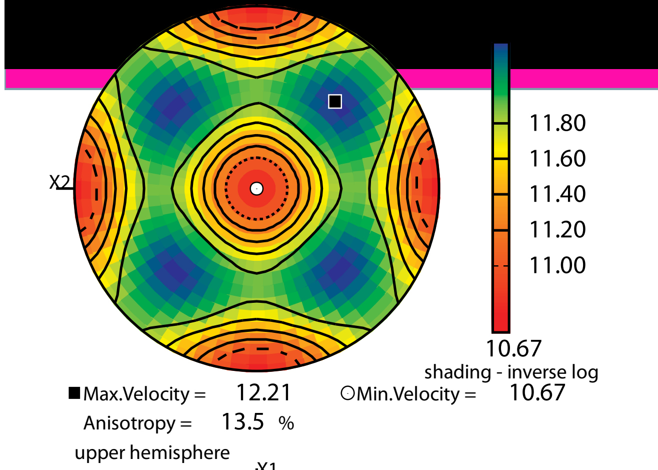


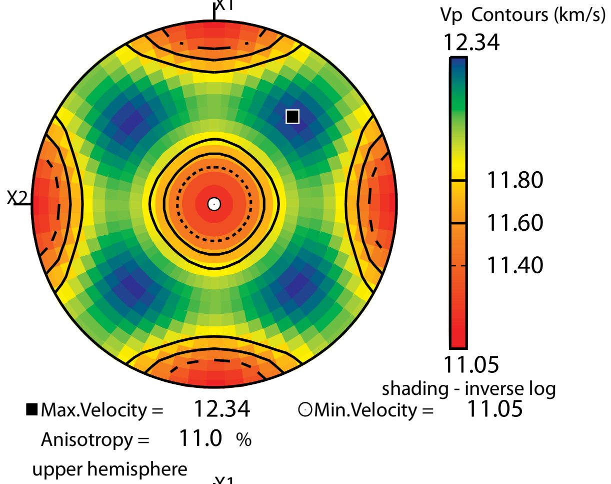
FeS

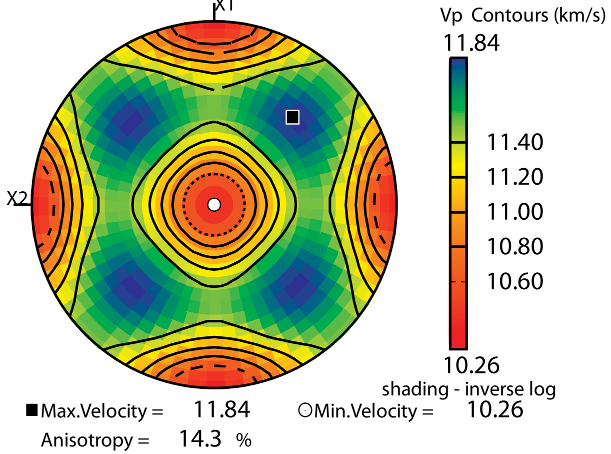


hcp-Fe









- Single crystal P-wave velocities for fcc-Fe, fcc-Fe$_3$S and c) fcc-Fe$_3$Ni projected onto a sphere at inner core conditions with the colourscale denoting the P-wave velocity.

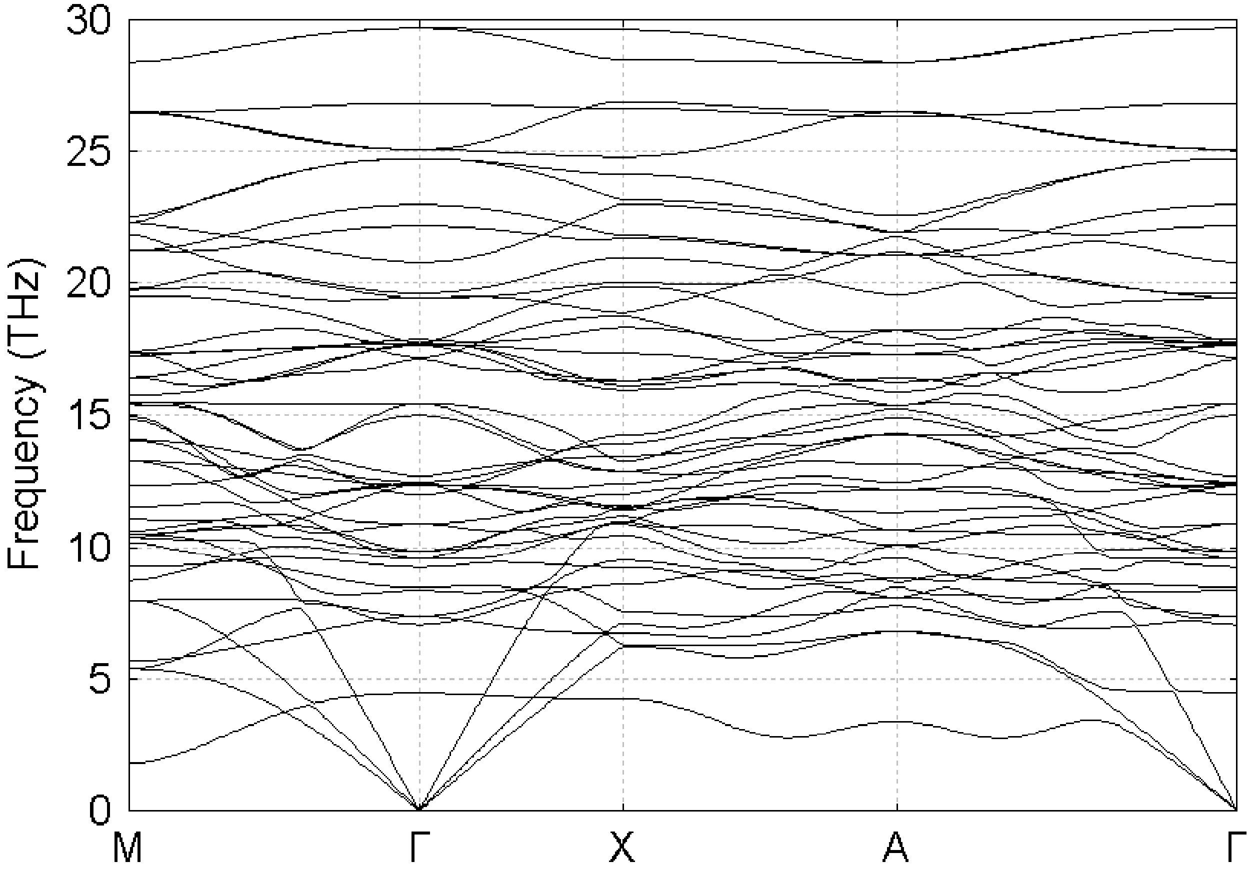
  (Unicef Careware, Mainprice, 1990).

- P-wave anisotropy 10-15%

- But not achievable along mutually perpendicular directions

Phonon dispersion for *bcc-Fe* with C

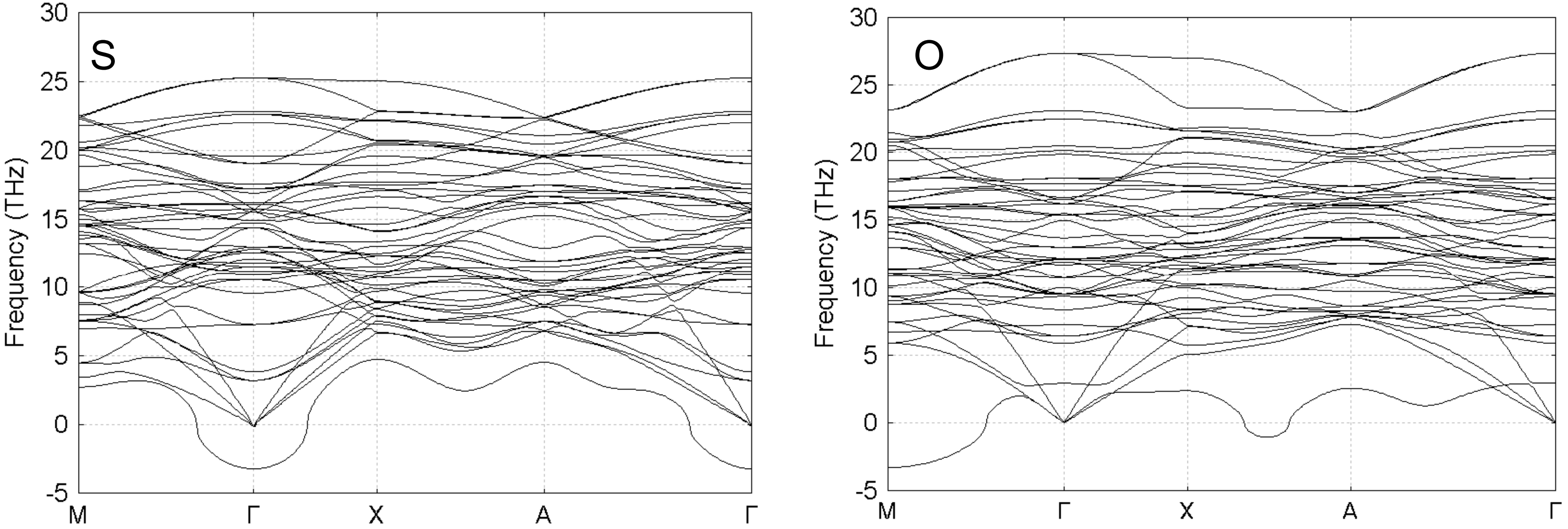
P = 330 GPa



- **Unstable at low concentrations; stable with 4.73 wt. % C**
- **hcp unstable at this concentration, so cannot compare F**

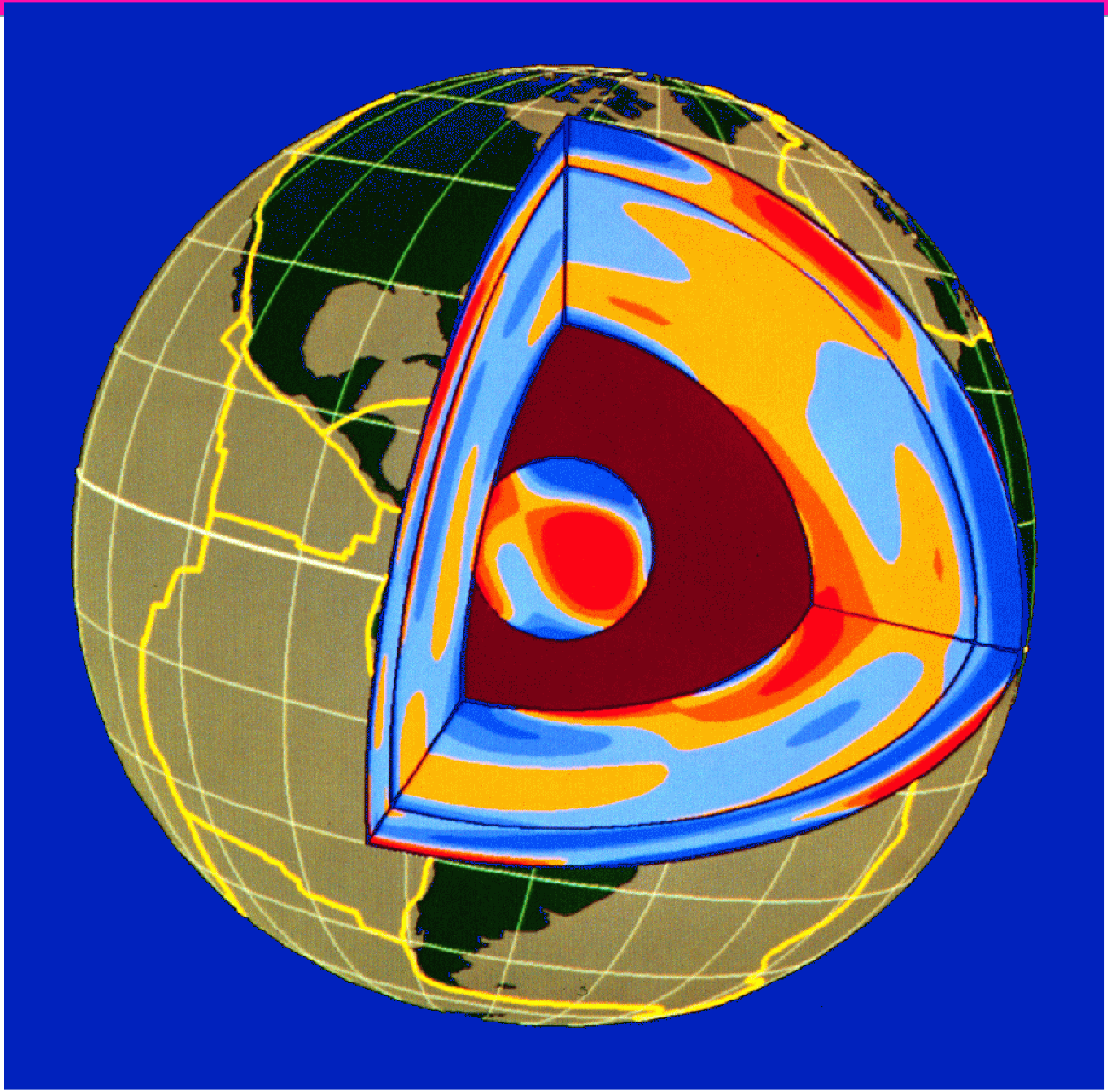
Phonon dispersion for *bcc-Fe* with S or O

P = 330 GPa

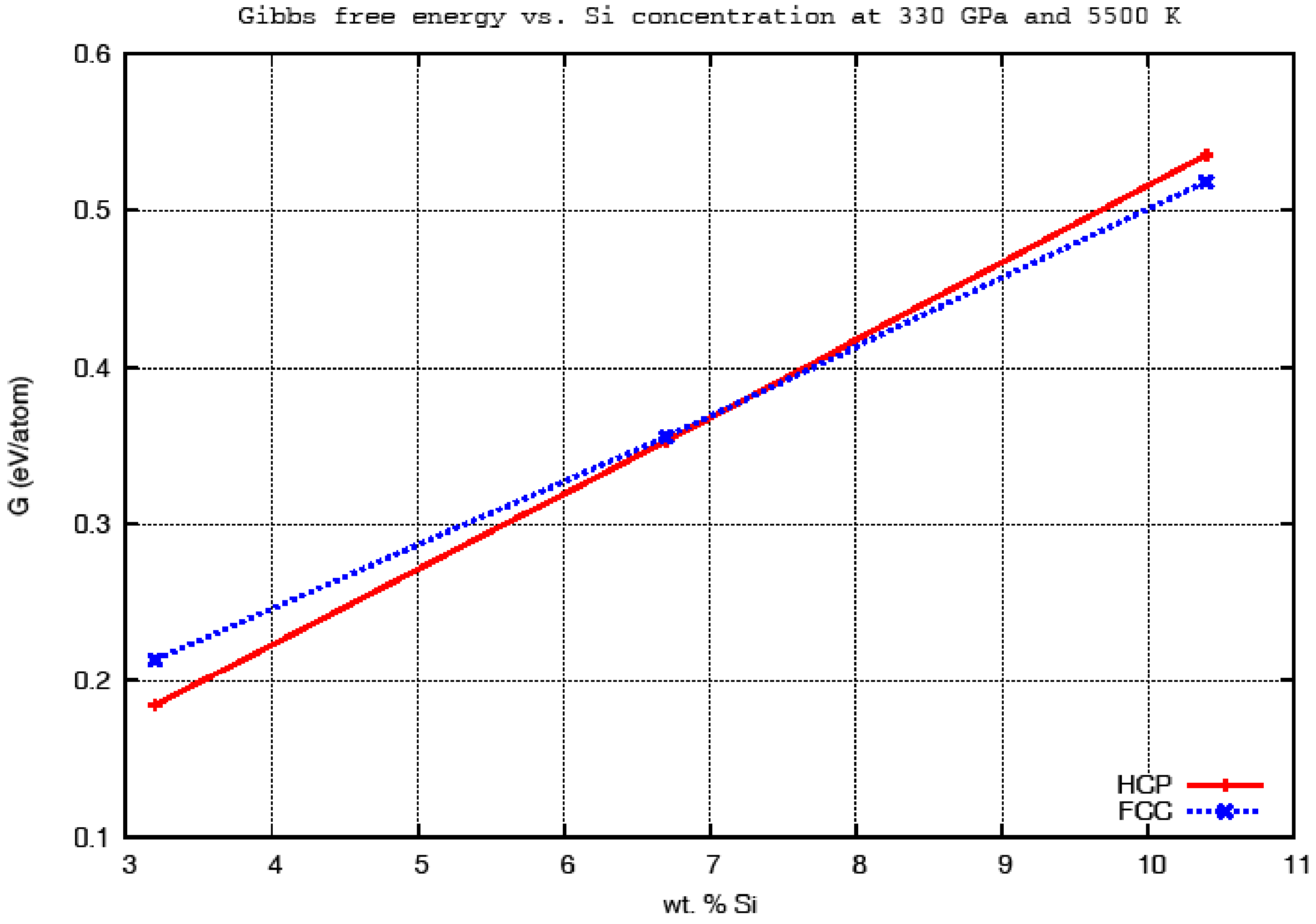


Unstable at all tested concentrations
(<18.75 atm. % ≡ 11.7 wt% S, 6.2 wt% O)

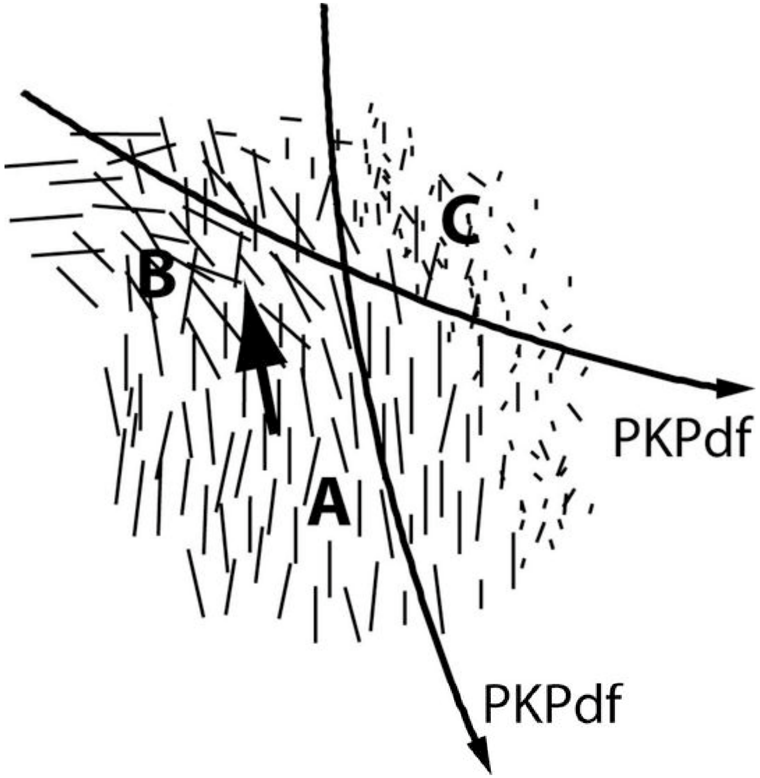
The Core: the only way out is in…….



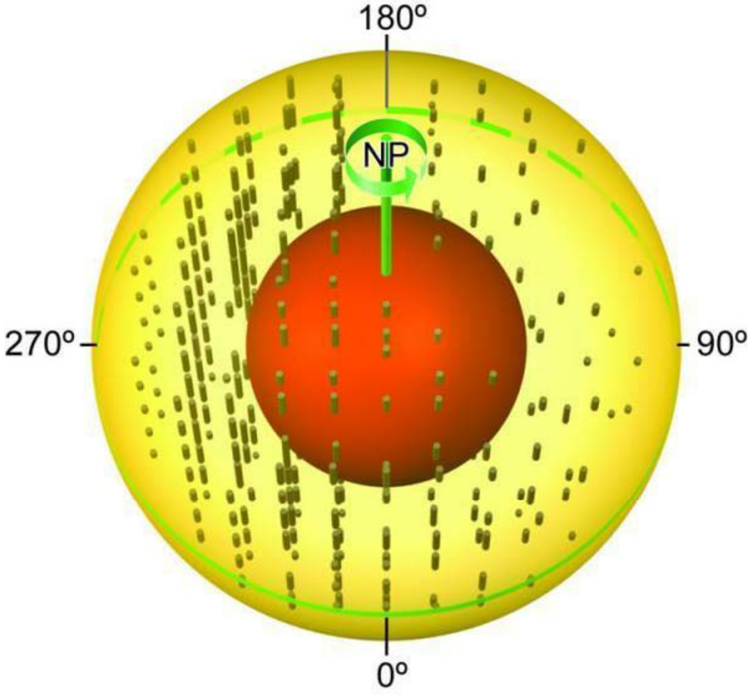
Stability of Fe at 330 GPa and 5500 K



Can we match seismic anisotropy?

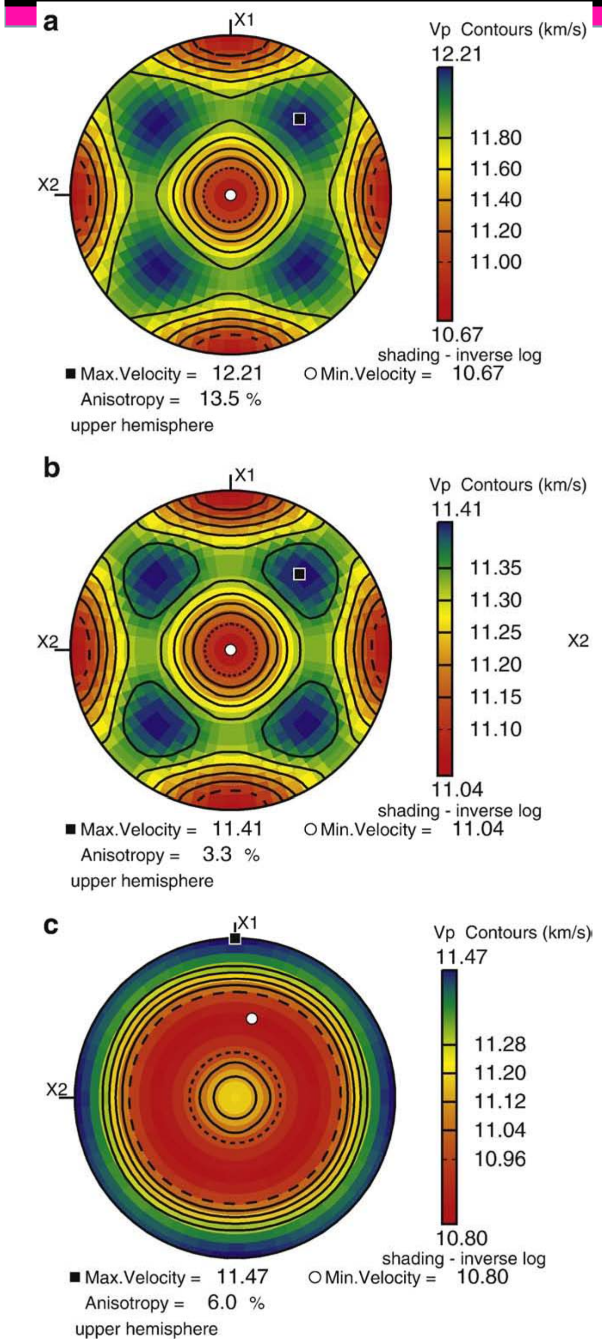


Tkalčić H. (2010)



Sun & Song 2008

The Core: the only way out is in…….



Single crystal P-wave velocities for:

a) fcc-Fe
b) bcc-Fe
c) hcp-Fe

Max anisotropy 13.5%, 3.3% and 11.47%
But not mutually perpendicular directions

For fcc-Fe:

- ~1% <110>, ~3% <111> and 6% <100>
- Significant to full alignment required
- For <111>, increase anisotropy by layering

For bcc-Fe:

- the maximum anisotropy <2%
- so anisotropy could not be alignment alone

For hcp-Fe:

- ~3% with c-axis in equatorial plane
- need full alignment.