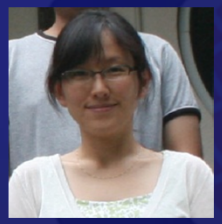
High-pressure physics of the Earth and beyond



Taku Tsuchiya

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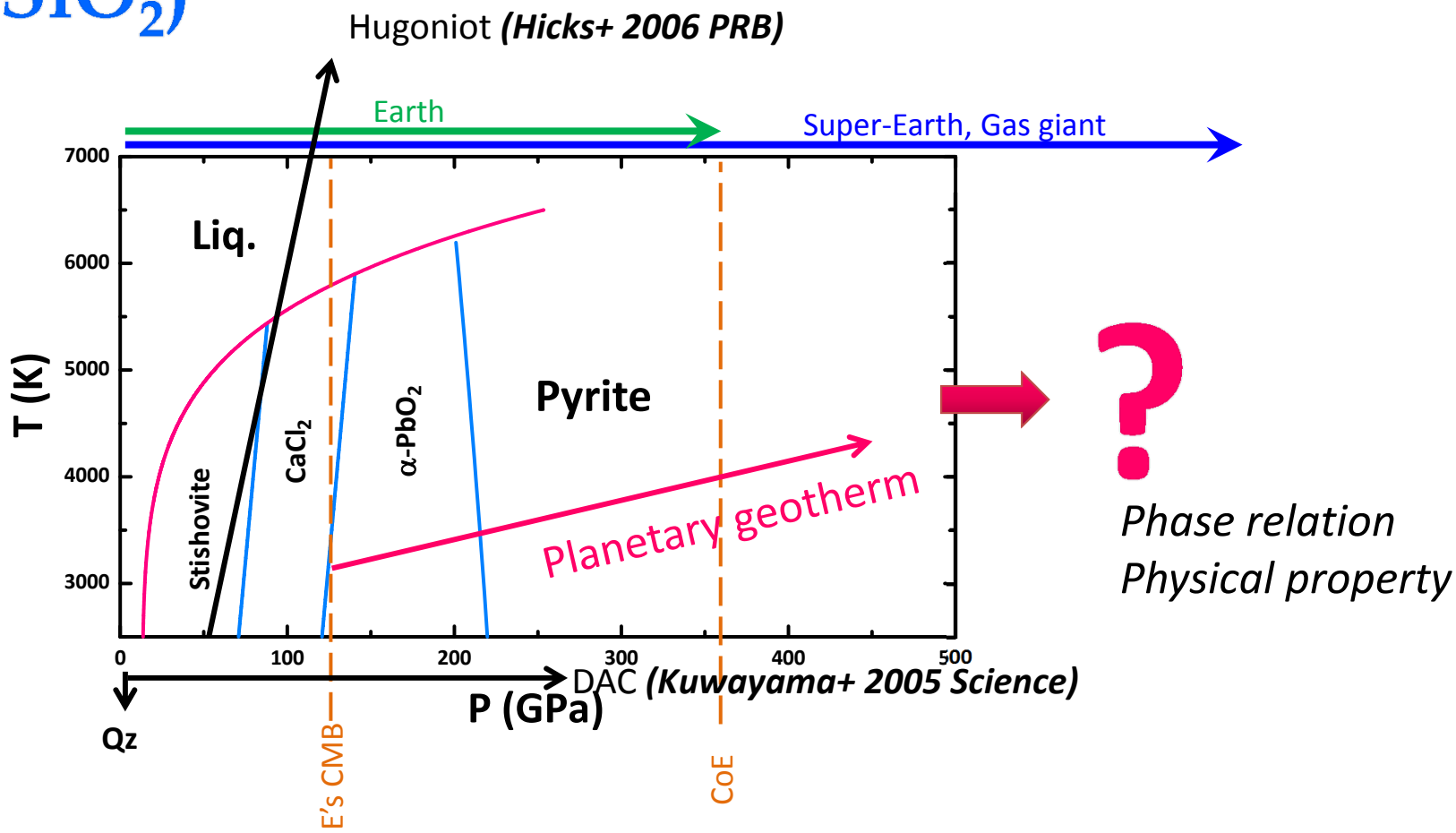
EHIME UNIVERSITY GRC GEODYNAMICS RESEARCH CENTER

Global COE DEEP EARTH MINERALOGY
EHIME UNIVERSITY JASRI, UNIV.TOKYO, SUNY

High-P,T phase relation of Earth materials (ex. SiO_2)



- Experimental investigations currently almost impossible
  - ***Ab initio* theoretical computation method**

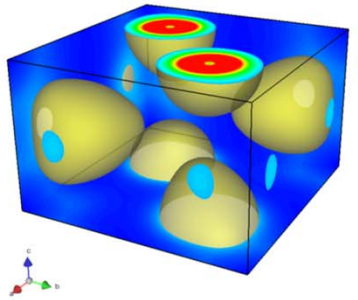
Ab Initio (first principles) Earth and Planetary Sciences

(*i*) Structural exploration

--- *Molecular dynamics*

(*ii*) Vibrational, thermodynamic property

--- *Lattice dynamics*



(*iii*) Elastic property

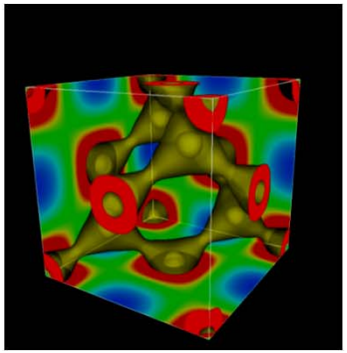
--- *Stress-strain theory*

(*iv*) Transport property

--- *Atomic, thermal, electrical conductivity*

(*v*) Mechanical property

--- *Shear response*



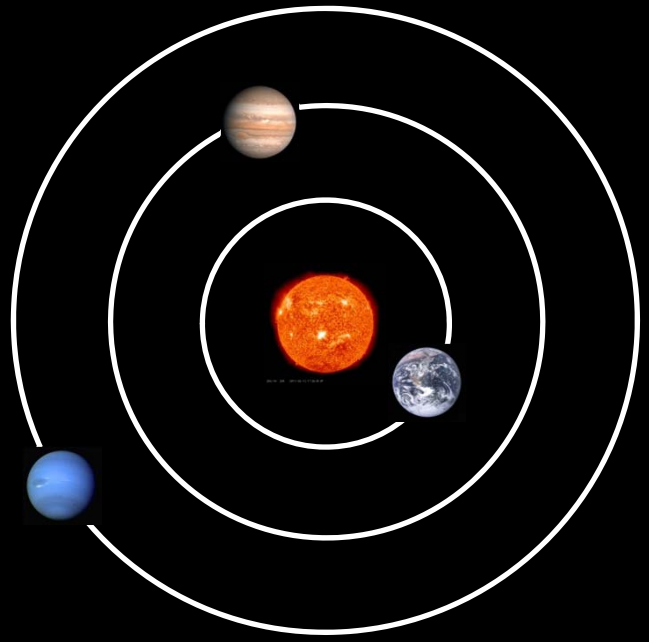
1. Fundamental methodologies of the ab initio electronic structure calculation method

2. Applications to high-pressure mineral physics and Earth & planetary interiors

   - Phase relations including melting
   - Electronic property
   - Transport property

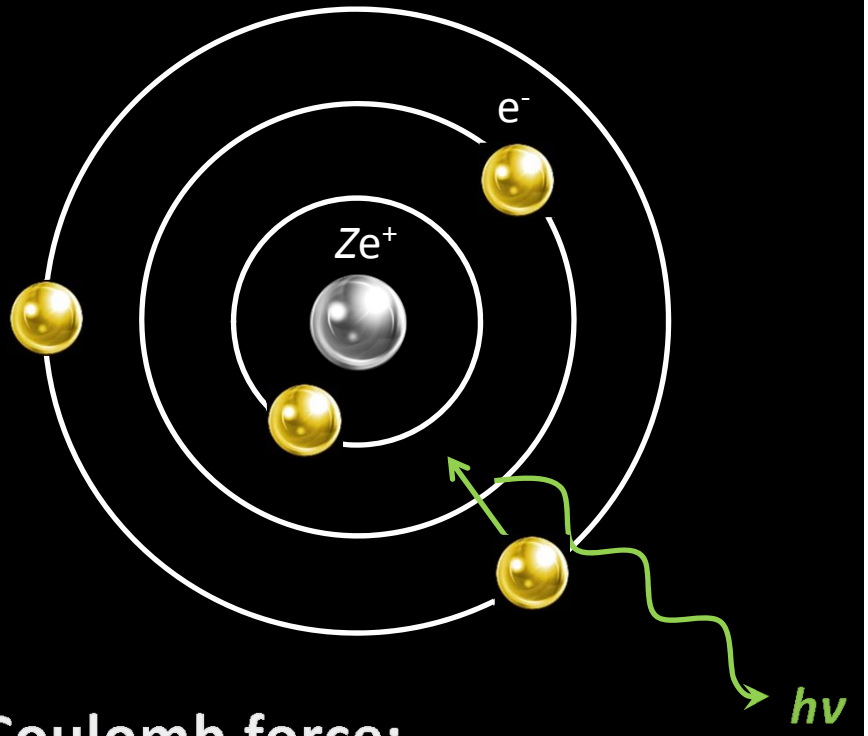
A.U.

(Astronomical Unit)



a.u.

(Atomic Unit)



Gravity force:

$$\mathbf{F}(\mathbf{r}) = -\frac{Gm_1m_2}{r^2}\frac{r}{\mathbf{r}}$$

Coulomb force:

$$\mathbf{F}(\mathbf{r}) = -\frac{1}{4\pi\varepsilon_0}\frac{q_1q_2}{r^2}\frac{r}{\mathbf{r}}$$

Central force

Schrödinger equation

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2 \cdots)\Psi(\mathbf{r}_1, \mathbf{r}_2 \cdots) = E\Psi(\mathbf{r}_1, \mathbf{r}_2 \cdots)$$

$\hat{H}$: Hamilton operator (Hamiltonian)

Ψ: Wave function (Eigen vector)

E: Total energy (Eigen value)

Eigenvalue problem

Quantization

$$\hat{p} = -i\hbar\nabla \quad \text{(Momentum)}$$

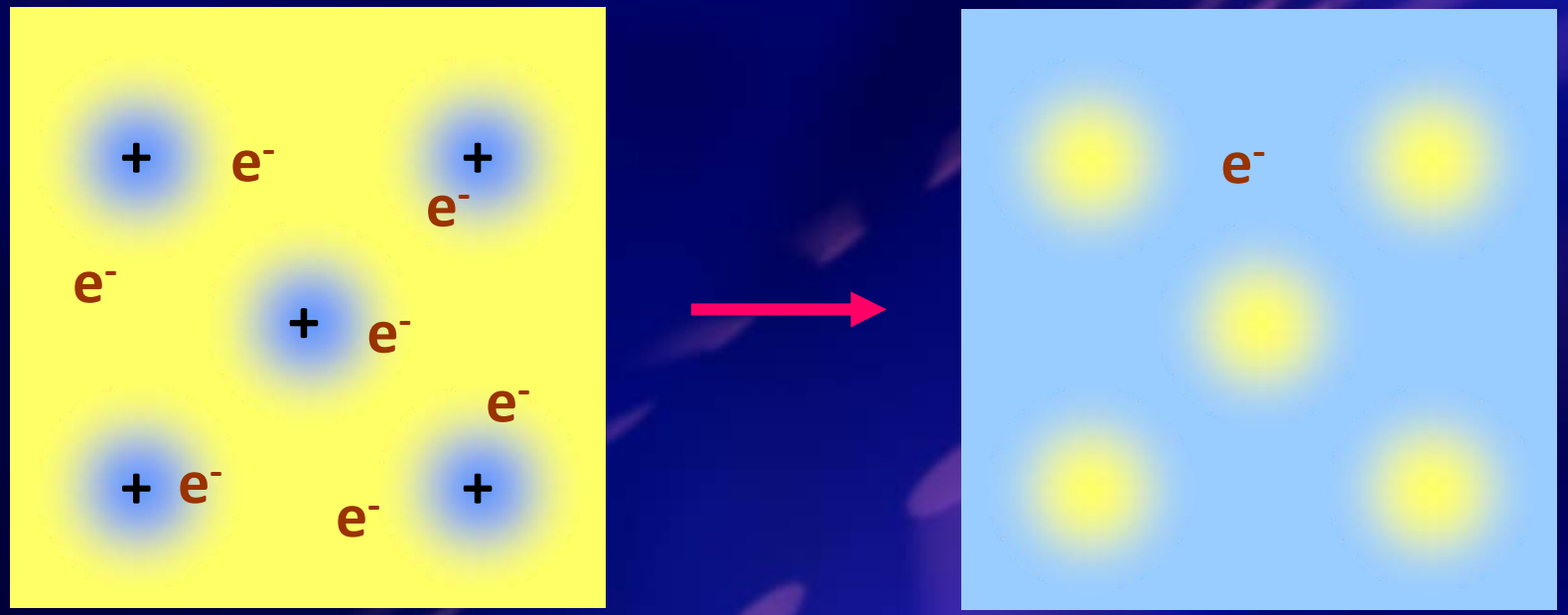
$$\hat{E} = i\hbar\partial/\partial t \quad \text{(Energy)}$$

Many-electron system

Interacting electrons

One electron in an effective potential

Ψ
E



ϕ_i
ε_i

$$\left[-\frac{\hbar^2}{2m}\Delta + V_{\mathrm{n}}[n(\mathbf{r})] + V_{\mathrm{H}}[n(\mathbf{r})] + V_{\mathrm{XC}}[n(\mathbf{r})]\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}),$$

$$n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$$

Kohn-Sham equations (DFT)

(Hohenberg & Kohn, 1964; Kohn & Sham, 1965)

Density Functional Theory (DFT)

One-electron Hamiltonian

$$\widehat{h_i} = -\frac{\hbar}{2m}\Delta + V_n[n(\mathbf{r})] + V_H[n(\mathbf{r})] + V_{XC}[n(\mathbf{r})]$$

Kinetic energy

Coulomb potential between electrons and nuclei

Coulomb potential between electrons

Quantum many-body effects

II

Exchange-correlation potential

Charge density

$$n(\mathbf{r}) = \sum_i \left| \phi_i(\mathbf{r}) \right|^2$$

Angular component of a wavefunction in a central force field

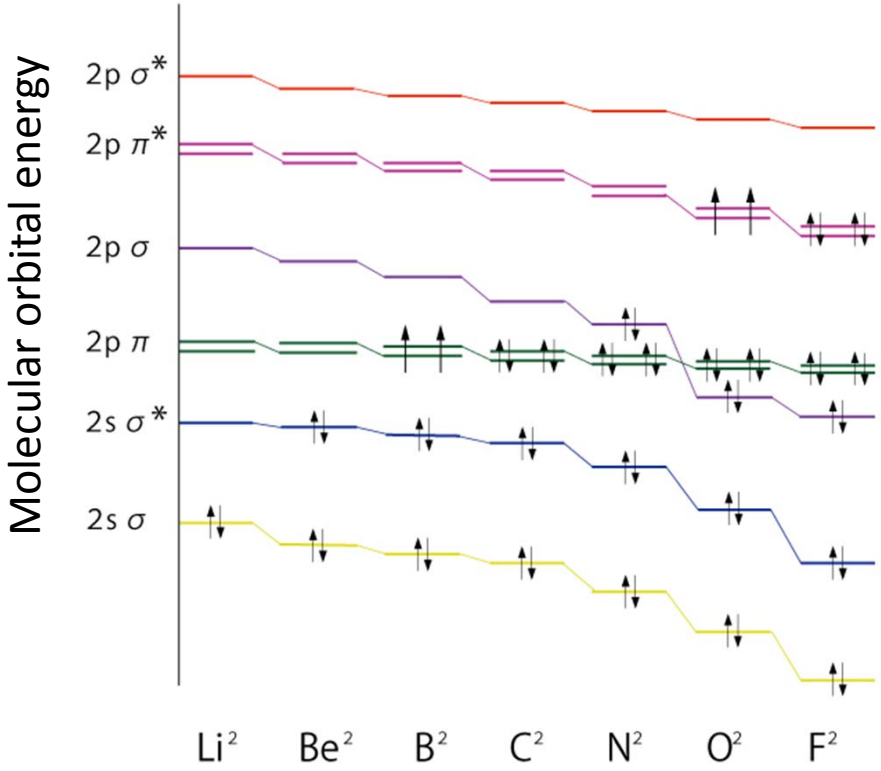
(Coulomb potential) $\propto 1/r$

= Spherical harmonics $\Phi_{l,m}$

l: angular momentum quantum number (s, p, d, f)

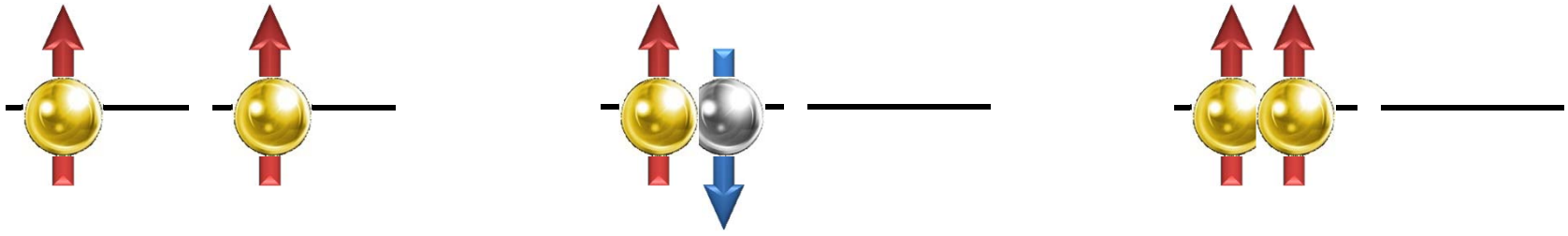
m: magnetic quantum number

+ spin quantum number (up or down)



XC (exchange-correlation) potential (V_{XC})

Electron (fermion) → Quantum many-body effects



E_I < E_{II} << E_{III}

Hund's rule

Pauli's exclusion principle

Local density approximation (LDA)

V_{XC} determined for the homogeneous electron gas, which can be calculated precisely, is applied also to general systems.

↑

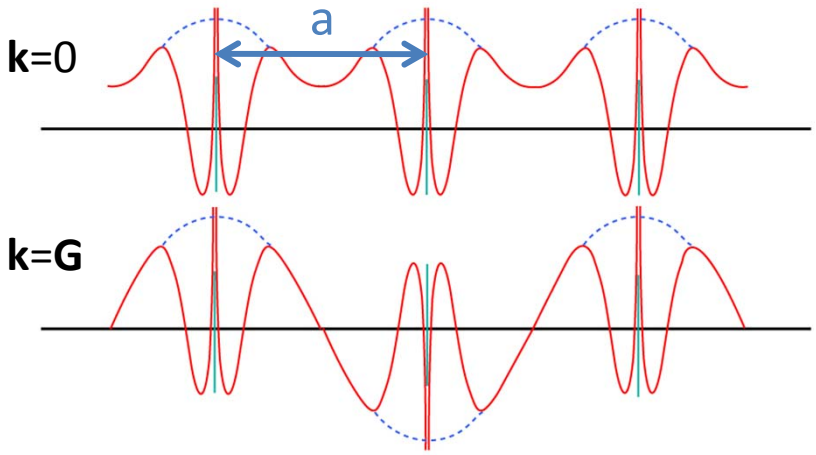
Quantum Monte-Carlo

Energy level to energy band

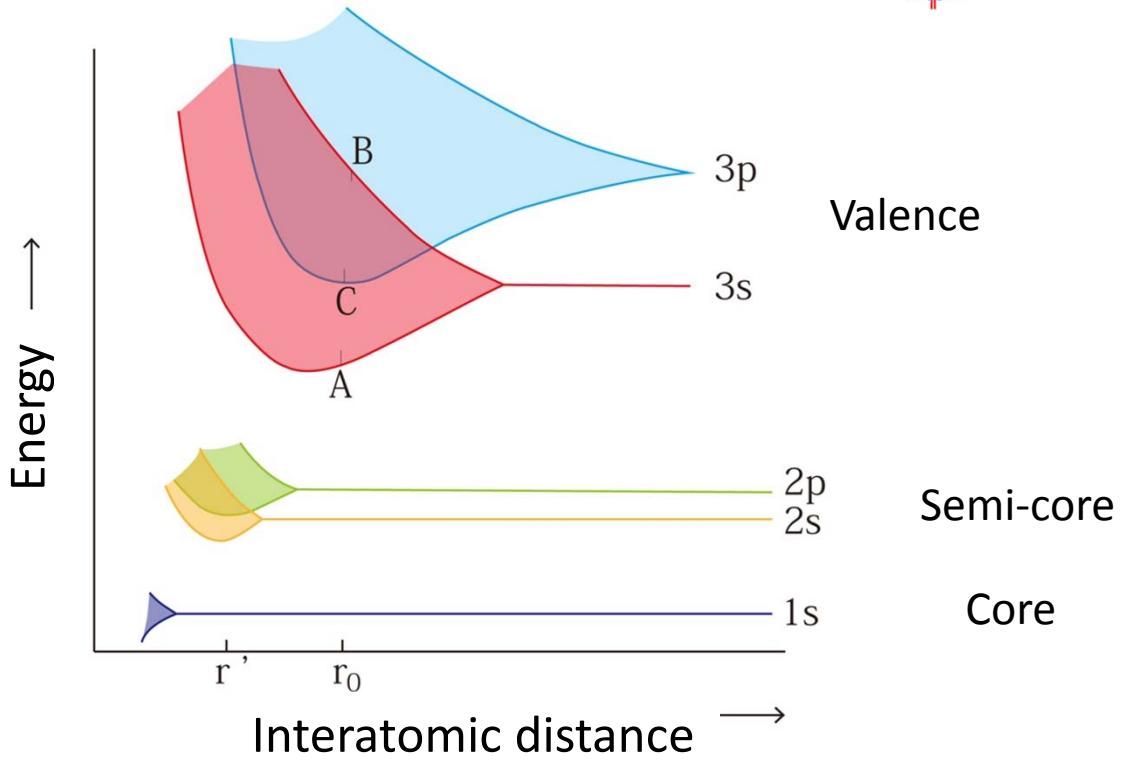
Bloch theorem

(Periodic boundary condition)

$$\psi_{\mathbf{k}}(\mathbf{r}) = a(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$$

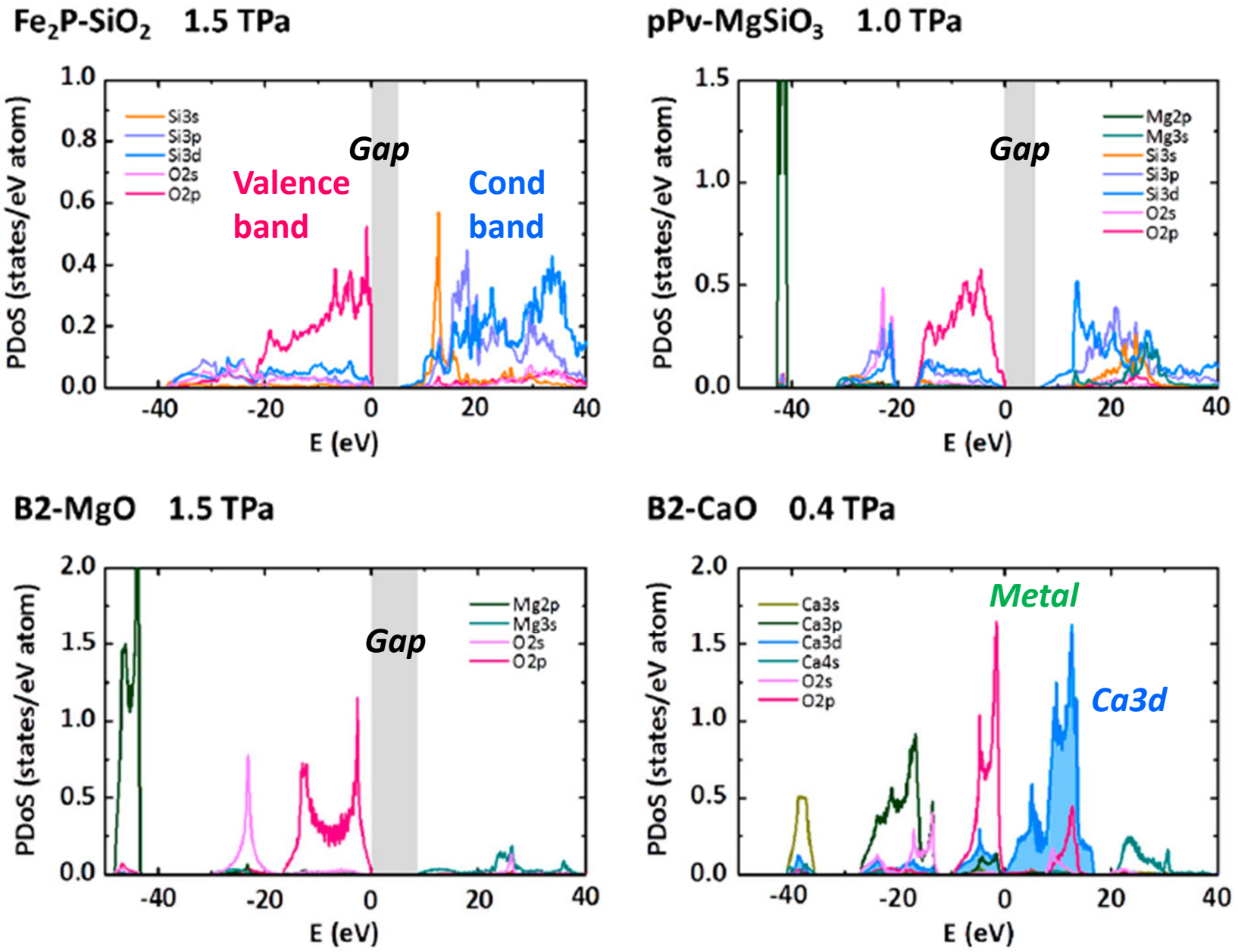


k-dependency of the energy level
= Energy band



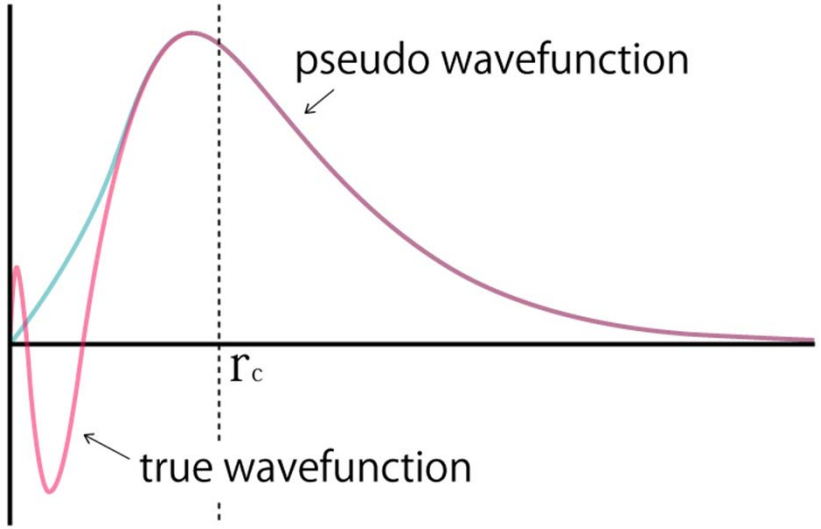
Electronic density of states

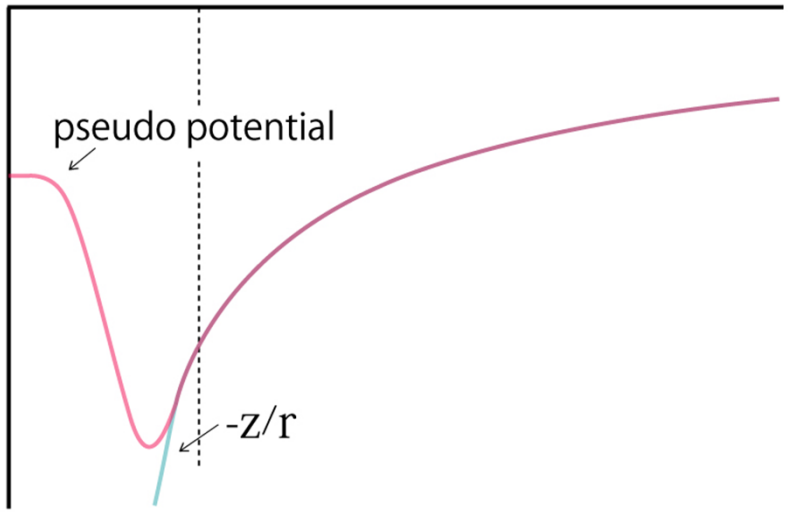
Tsuchiya & Tsuchiya (2011) PNAS



Pseudo-potential approximation

- Valence electrons only contribute chemical bonding.
- Nuclei + Core electrons → Ion potential (with orthogonality of valence and core electrons)





PP is determined nonempirically to reproduce the true wavefunction correctly in the bonding region ($r > r_c$).

Self-Consistent Field (SCF) method

$$\hat{h}_i[n(\mathbf{r})]\,\phi_i(\mathbf{r}) = \varepsilon_i\,\phi_i(\mathbf{r})$$

ϕ_i depends on the Hamiltonian $\hat{h}_i[n(\mathbf{r})]$.

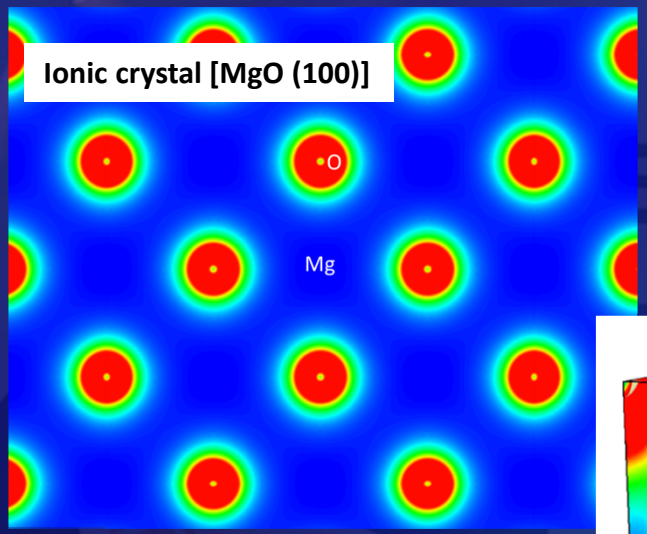
$\hat{h}_i[n(\mathbf{r})]$ depends on the total charge density $n(\mathbf{r})$.

$n(\mathbf{r})$ depends on the wave functions ϕ_i.

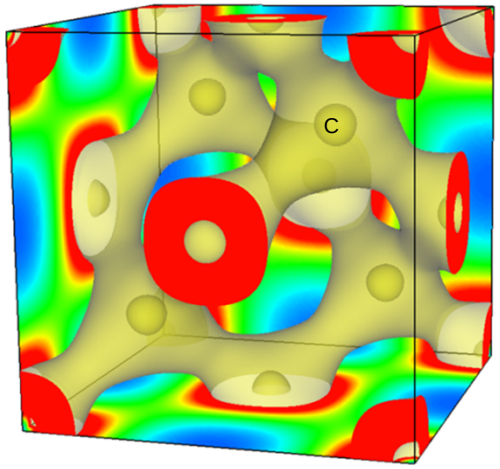
The equation is solved iteratively.

Valence charge density of some representative bond types

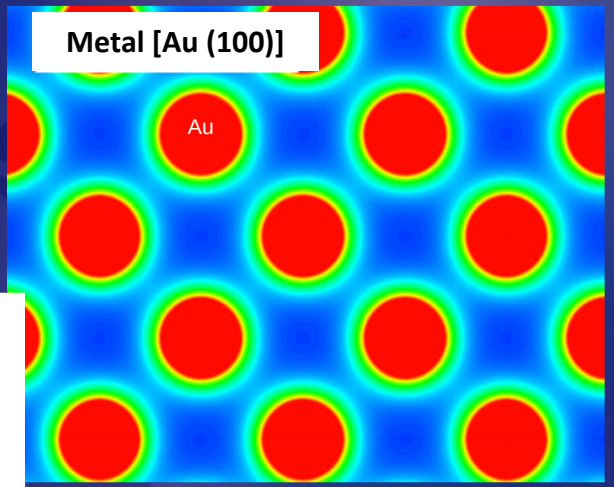
Ionic crystal [MgO (100)]



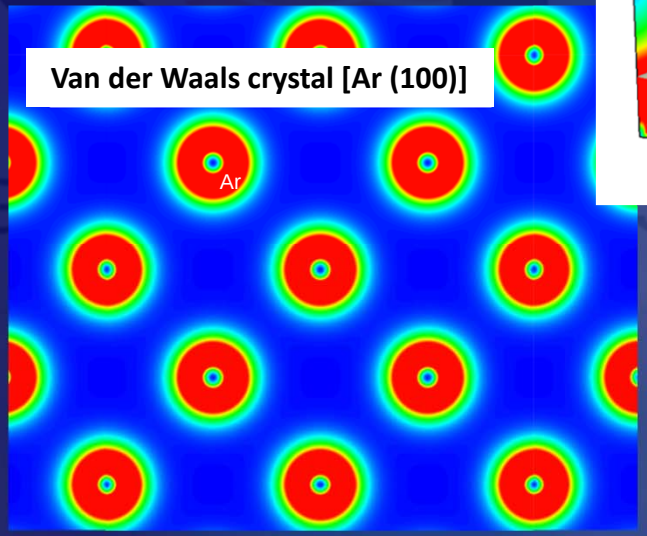
Covalent crystal [diamond]



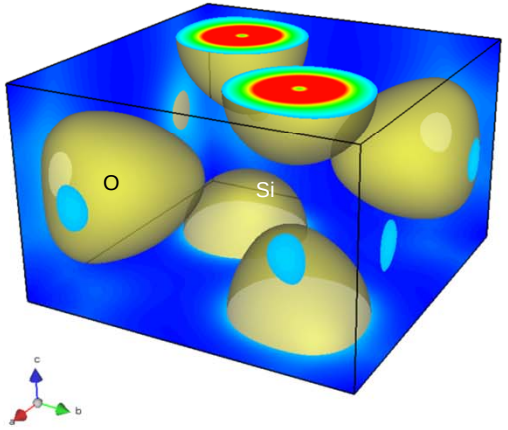
Metal [Au (100)]



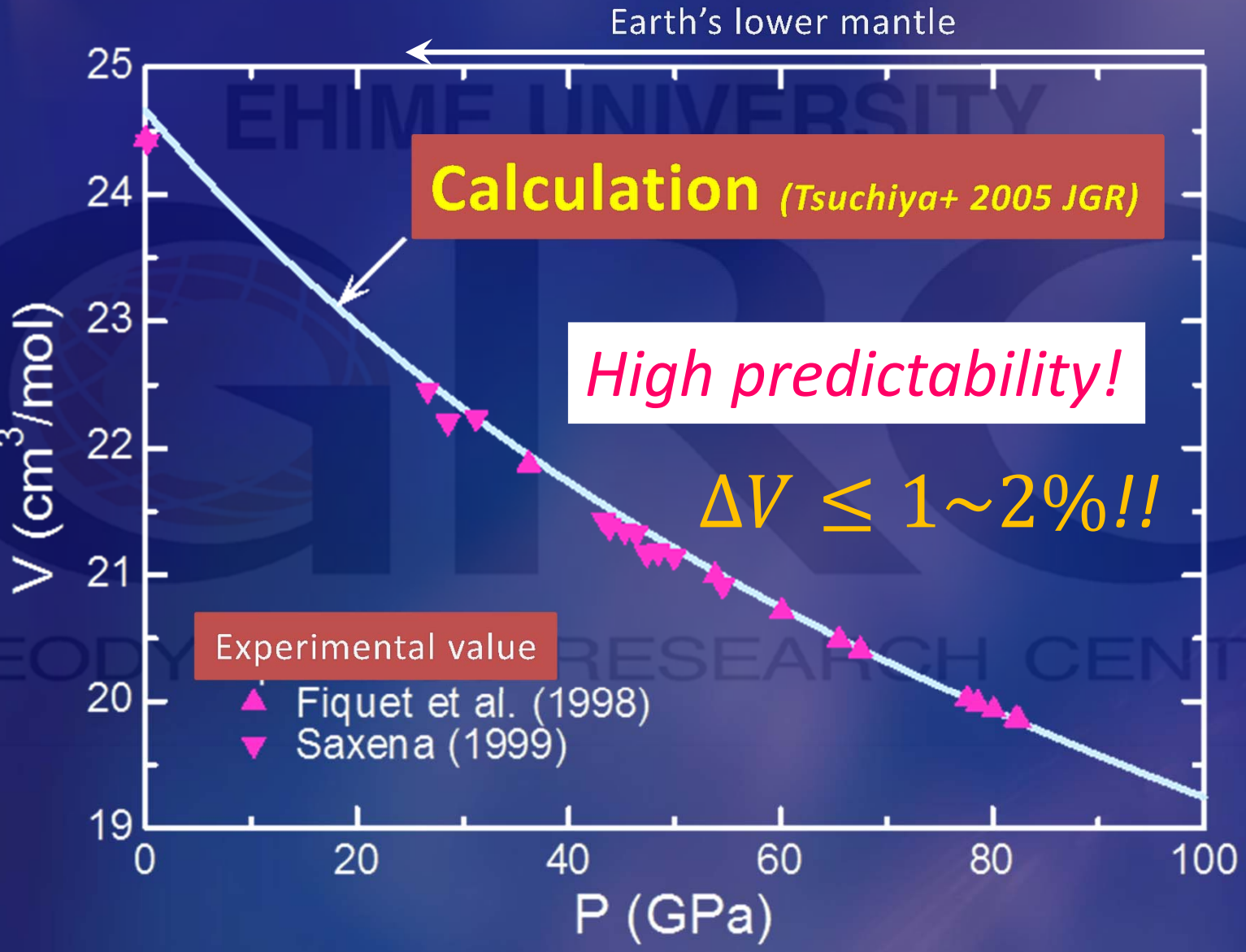
Van der Waals crystal [Ar (100)]



Ionic + covalent SiO_2 [Stishovite]



Compression curve of $MgSiO_3$ perovskite (A lower mantle constituent phase)



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Large scale computation

GRC-SRFC parallel clusters

次世代スーパーコンピュータプロジェクト
（文部科学省「最先端・高性能汎用スーパーコンピュータの開発利用」プロジェクト）

理研計算科学研究機構@神戸

http://jp.fujitsu.com

Atomic dynamics and temperature effects

DFT → Total energy of many-electrons system (E_{tot})

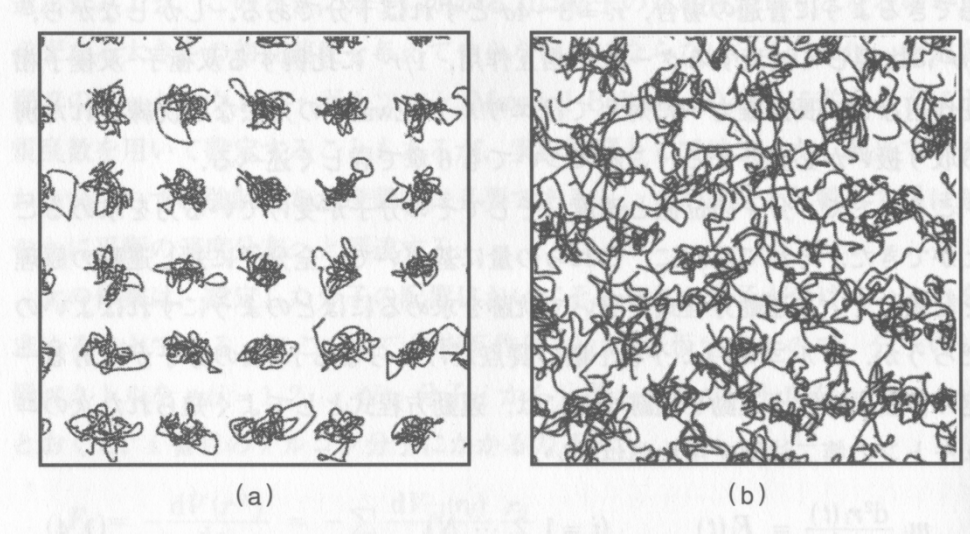
+ Hellman-Feynman theorem (perturbation theory)

$$\frac{\partial E_{tot}}{\partial \mathbf{r}_i}$$ (Force) → *Ab initio* molecular dynamics (MD)

$$\frac{\partial^2 E_{tot}}{\partial \mathbf{r}_i \partial \mathbf{r}_j}$$ (Force constant) → *Ab initio* lattice dynamics (LD)

Molecular Dynamics method

A method to investigate dynamical property of many-atom systems



Solid (a)
Liquid (b)

Time evolution is calculated by numerically integrating the Newton's equation of motion

$$\mathbf{x}_i(t+\Delta t) = \mathbf{x}_i(t) + \mathbf{v}_i(t)\Delta t + \frac{1}{2}\mathbf{a}_i(t)\Delta t^2$$

$$\mathbf{v}_i(t+\Delta t) = \mathbf{v}_i(t) + \frac{\mathbf{a}_i(t) + \mathbf{a}_i(t+\Delta t)}{2}\Delta t$$

Velocity-Verlet algorithm

$$\mathbf{a}_i(t) = \mathbf{F}_i(t)/m_i$$

Hellman-Feynman theorem

$$\frac{dE}{d\lambda} = \left\langle \psi(\lambda) \left| \frac{d\hat{H}}{d\lambda} \right| \psi(\lambda) \right\rangle$$

Force acting on an atom can be calculated directly from the SCF charge density.

→ **Force**

→ **Stress tensor** ***(Nielsen & Martin, PRB 1985)***

Macroscopic thermodynamic quantities

Temperature (Energy equipartition principle)

$$T = \frac{1}{3Nk_B}\sum_j m_j v_j^2$$

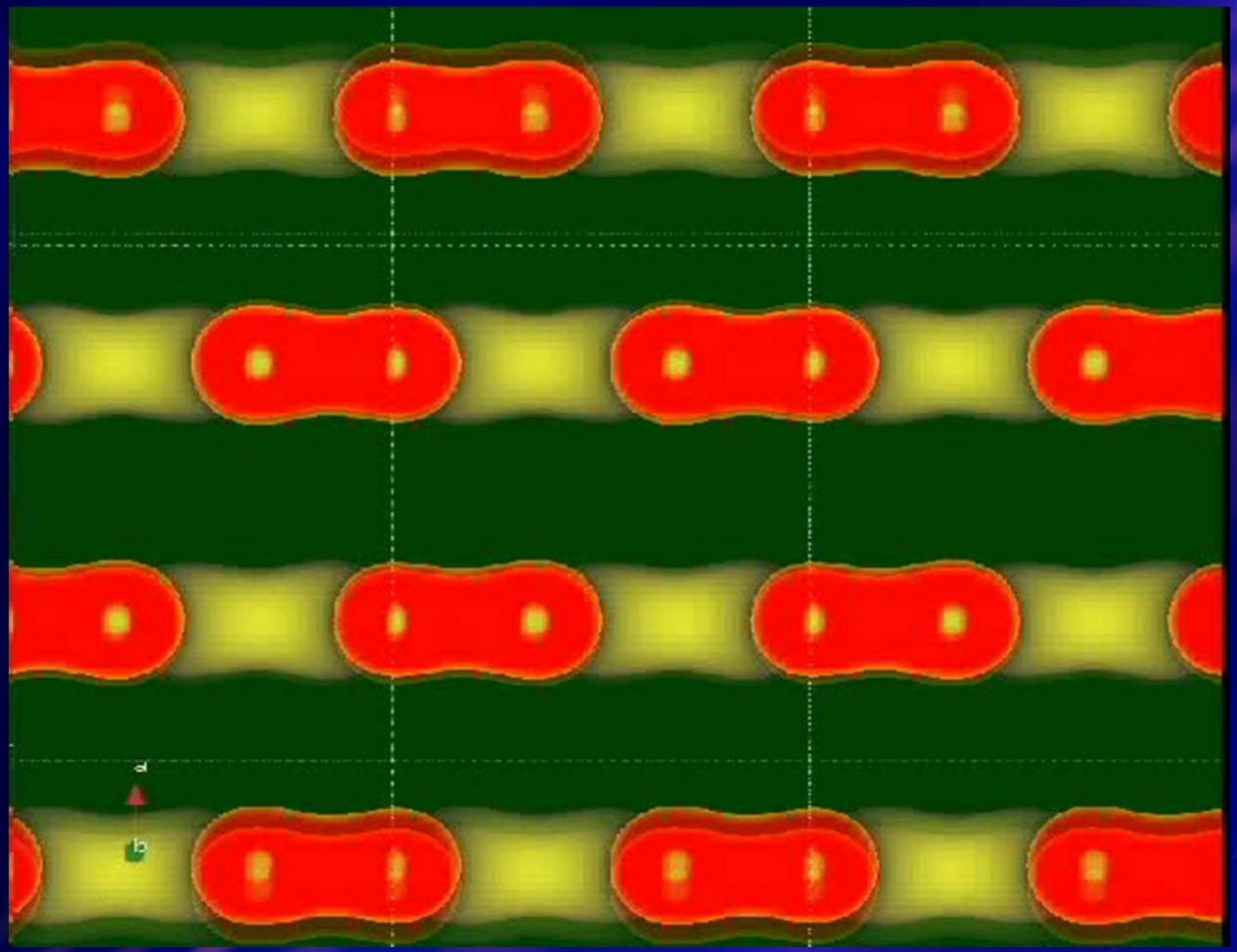
Pressure (Virial theorem)

$$P = P_{static} + \frac{Nk_BT}{V} - \frac{1}{3V}\sum_{i>j} \mathbf{F}_{ij} \otimes \mathbf{r}_{ij}$$

But not temperature dependence of heat capacity due to the classical Newton's dynamics (Dulong-Petit law)

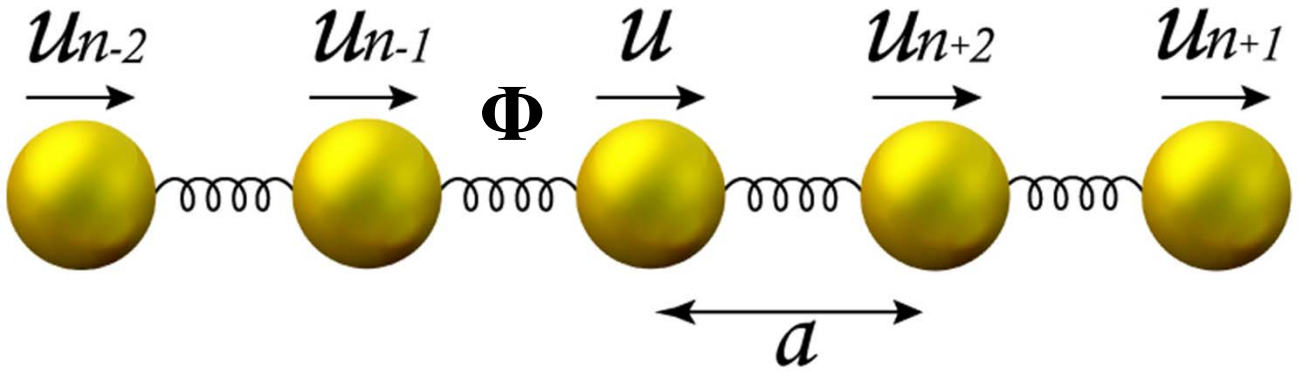
Graphite

[0001]



Graphite sp^2 → **(Hexa-)Diamond** sp^3

Lattice Dynamics Method



Harmonic approximation

Force (spring) constant matrix

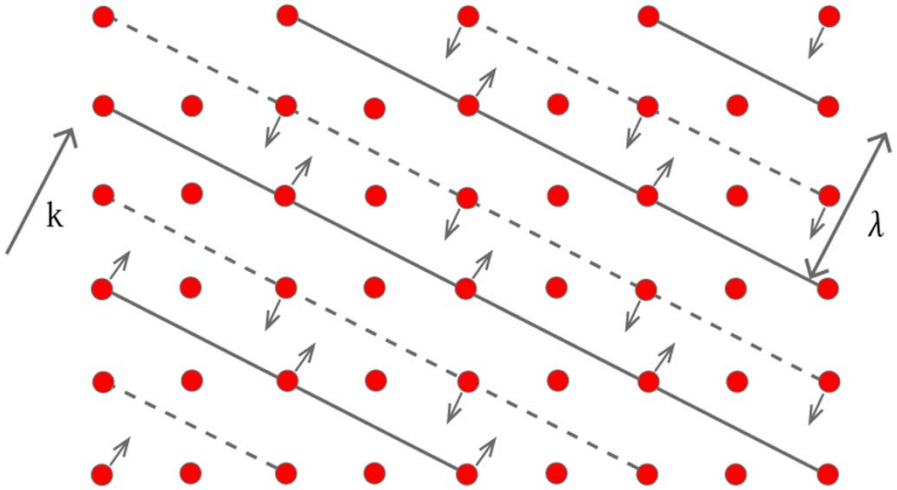
$$E^{harm} = \frac{1}{2} \sum_{ll',nn',\alpha\beta} \Phi^{\alpha\beta}_{nn'}(l,l') u^{\alpha}_{n}(l) u^{\beta}_{n'}(l') \qquad (\alpha,\beta = x,y,z)$$

Equation of motion

$$F^{\alpha}[\mathbf{r}_n(l)] = -\frac{\partial E^{harm}}{\partial u^{\alpha}_{n}(l)} = -\sum_{l',ll',\alpha\beta} \Phi^{\alpha\beta}_{nn'}(l,l') u^{\beta}_{n'}(l')$$

Solution $u^{\alpha}_{n}(l) = u^{\alpha}_{n}(\mathbf{q}) \exp[i\mathbf{q}\cdot\mathbf{r}(l) - i\omega t]$

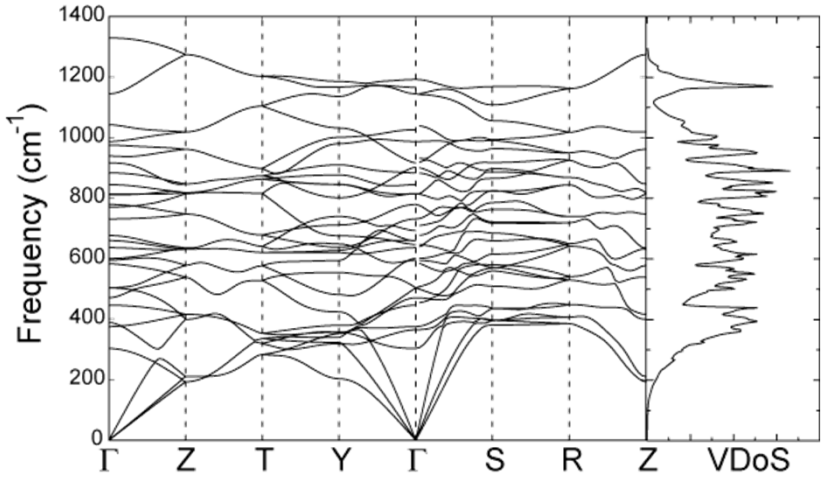
Dynamical matrix $$\mathbf{D}_{nn'}^{\alpha\beta}(\mathbf{q}) = \frac{1}{\sqrt{m_n m_{n'}}} \sum_l \mathbf{\Phi}_{nn'}^{\alpha\beta}(0,l) \exp[i\mathbf{q}\cdot(\mathbf{r}_0 - \mathbf{r}_l)]$$



$$\omega^2 u_n^\alpha(\mathbf{q}) = \sum_{n',\beta} \frac{\mathbf{D}_{nn'}^{\alpha\beta}(\mathbf{q})}{\sqrt{m_n m_{n'}}} u_{n'}^\beta(\mathbf{q})$$

Density Functional Perturbation Theory (DFPT)

(Baroni+ PRB 1987; RMP 2001)

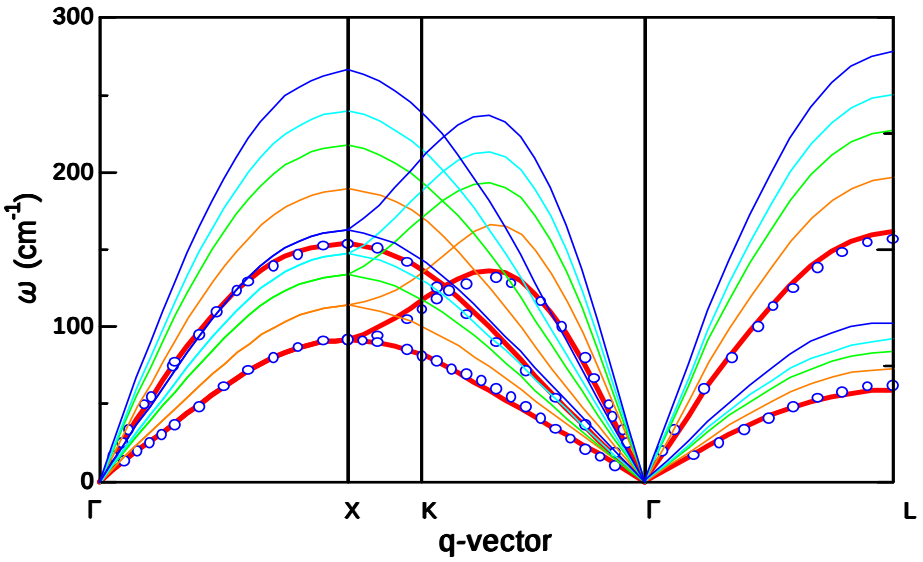


Phonon dispersion of $MgSiO_3$ pPv (P=120GPa)

Calculate the dynamical matrix based on the quantum perturbation theory

Phonon (quantized lattice vibration) **dispersion relation**

gold (Au)

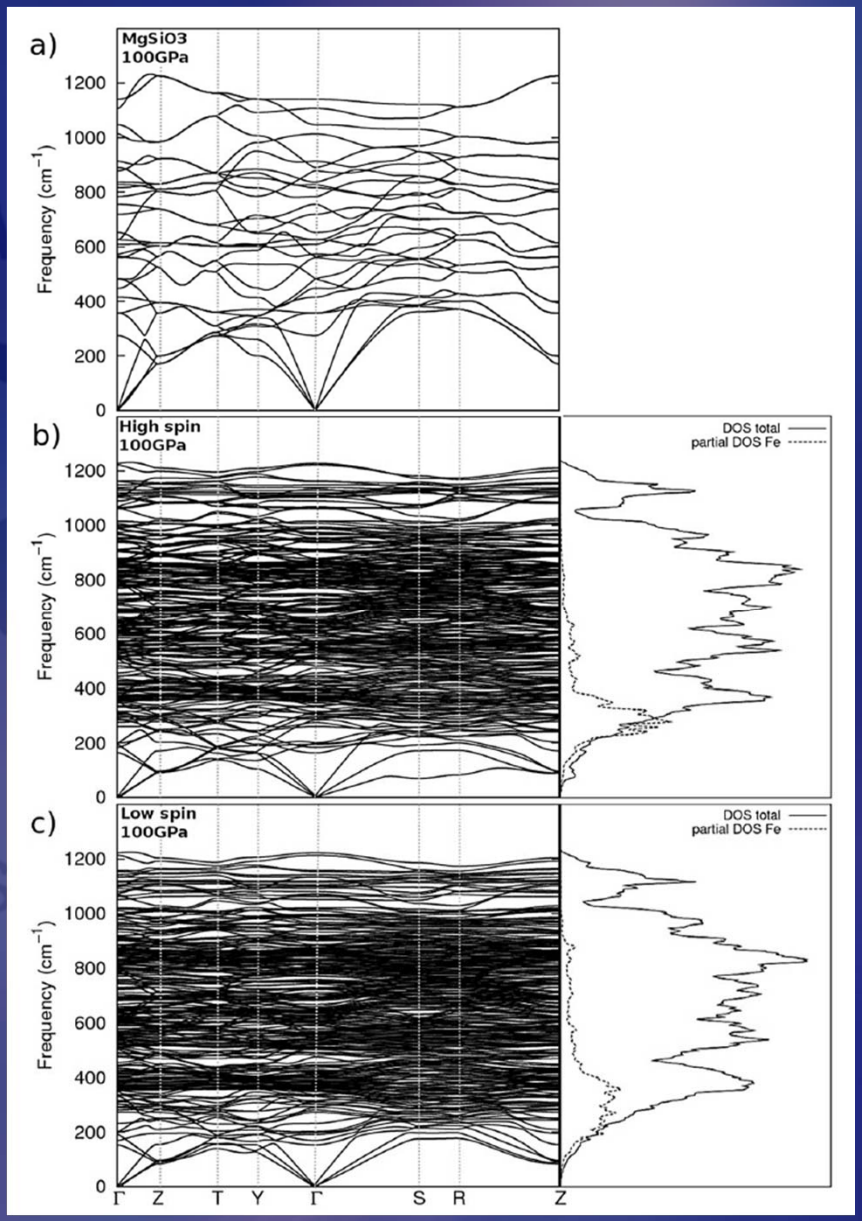


Calc

- V/V_0 =1
- 0.93
- 0.86
- 0.82
- 0.79
- Expr. (V/V_0=1) (Neutron Scatering)

Tsuchiya (2003) JGR

Silicates and solid solutions



$(Mg,Fe)SiO_3$ Metsue & Tsuchiya (2011,2012)

Quasi-Harmonic Approximation (QHA)

Phonon Helmholz free energy

$$F_{ph}(V,T) = \frac{1}{2}\sum_{\mathbf{q},j} h\omega_j(\mathbf{q},V) + k_B T \sum_{\mathbf{q},j} \ln\left[1 - \exp\left\{-\frac{h\omega_j(\mathbf{q},V)}{k_B T}\right\}\right]$$

Total Helmholz free energy

$$F(V,T) = U_{stat}(V) + F_{ph}(V,T) + F_{el}(V,T) + \cdots$$

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

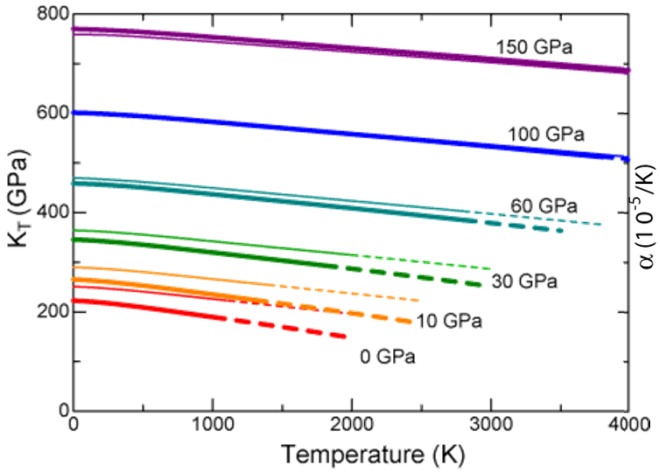
Entropy $$S = -\left[\frac{\partial F}{\partial T}\right]_V$$

Other thermodynamic functions including

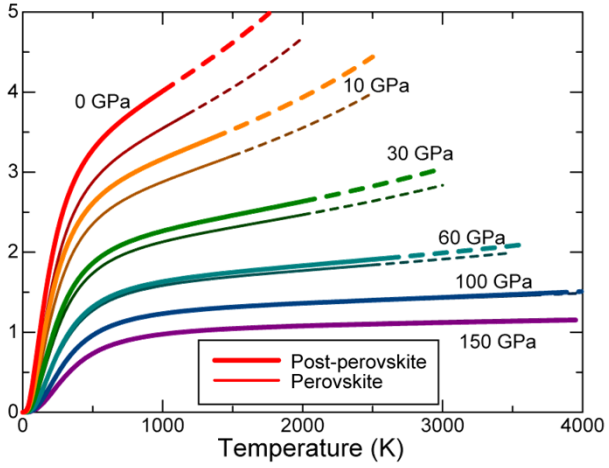
$$G(P,T) = F(V,T) + P(V,T)V$$

Crystal thermodynamics (e.g., $MgSiO_3$ Pv and PPv)

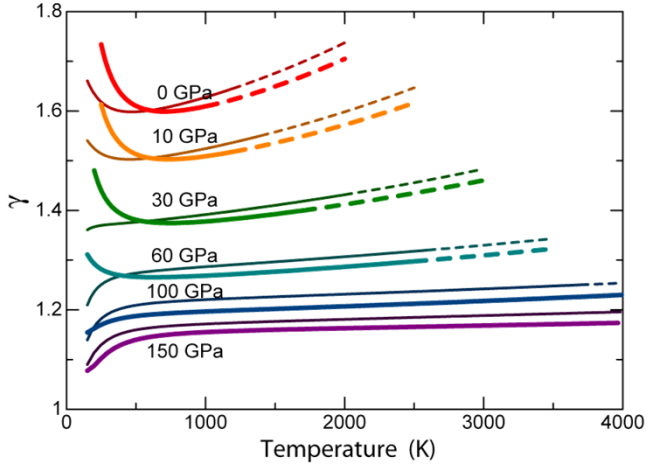
Isothermal bulk modulus K_T



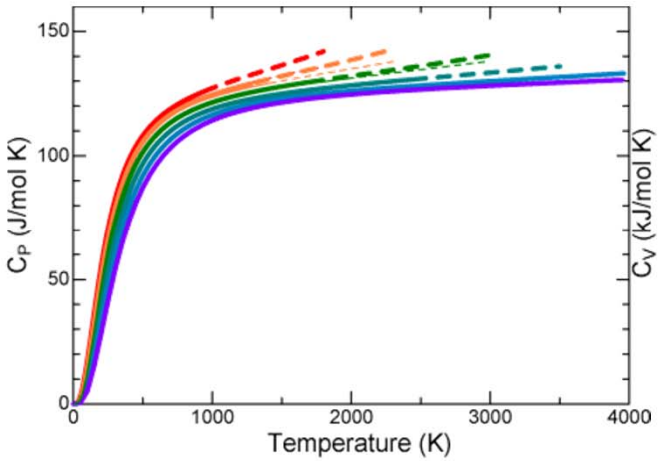
Thermal expansion coefficient α



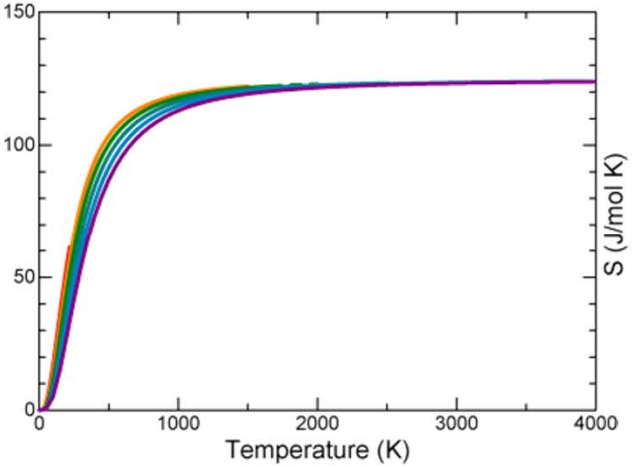
Grüneisen parameter γ



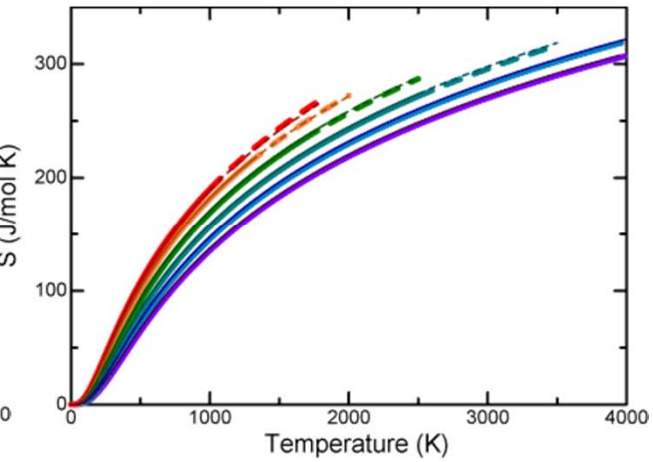
Heat capacity C_p



Heat capacity C_v

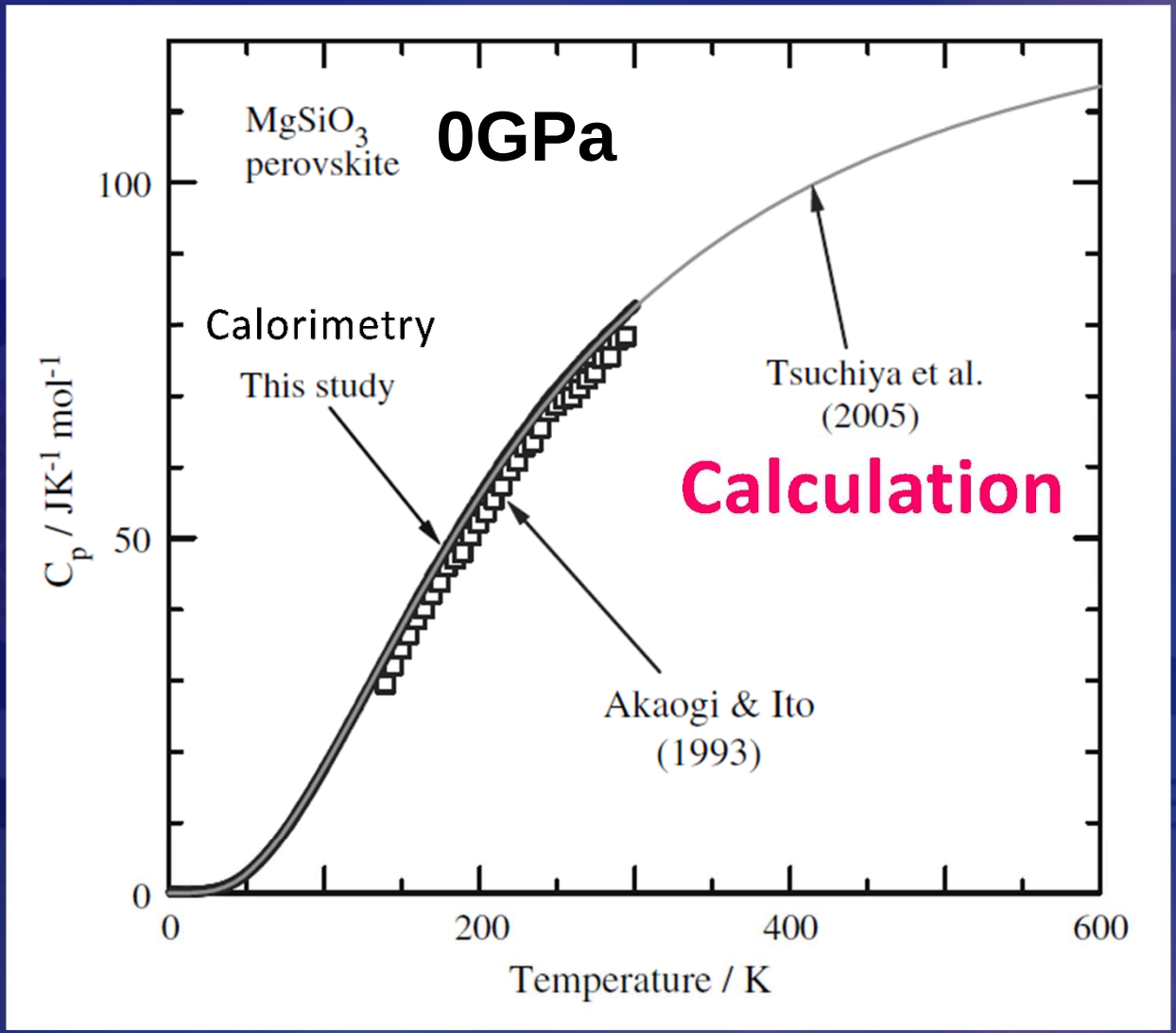


Entropy S



Tsuchiya+ (2005) JGR

Akaogi+ (2008) Phys Chem Miner

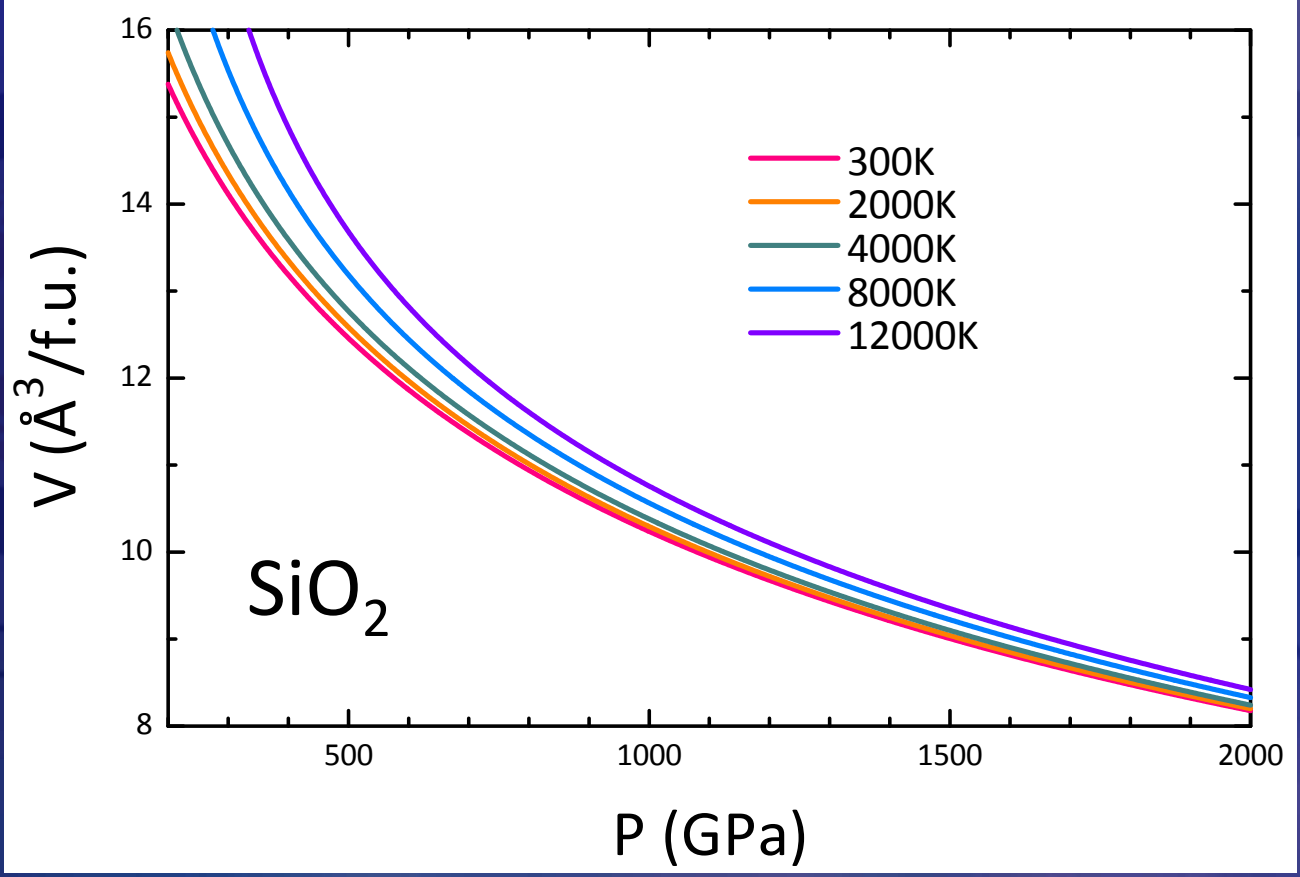


Excellent agreement

P-V-T equation of state up to ultrahigh *P,T*

$$P(V,T) = P_{static}(V) + P_{thermal}(V,T)$$

$$P_{thermal}(V,T) = P_{ph}(V,T) + P_{el}(V,T) + P_{mag}(V,T)$$

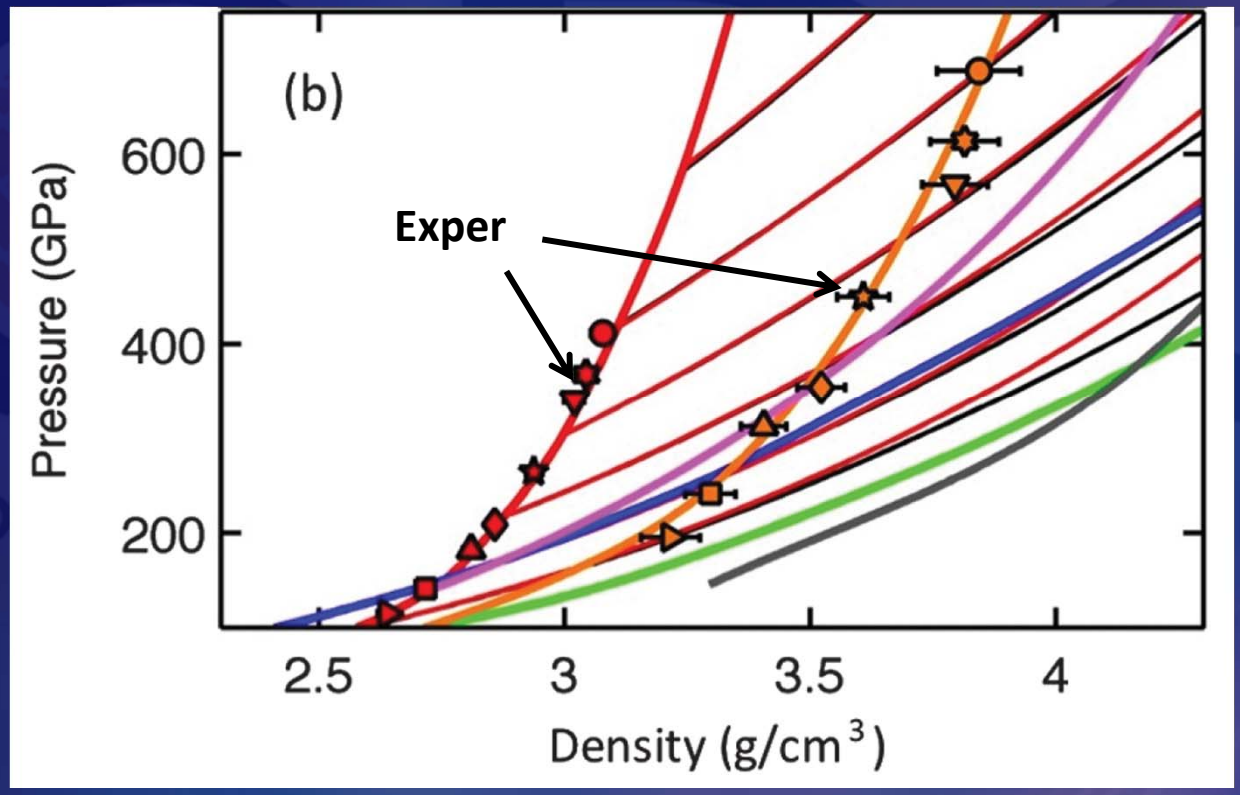


Hugoniot condition $H = E - E_0 + 1/2(P + P_0)(V - V_0) = 0$

How accurate are calculated EoS?

e.g., EoS of H_2O

Experimental confirmation in the TPa condition is quite difficult.
Laser or magnetic shock technique seems hopeful.

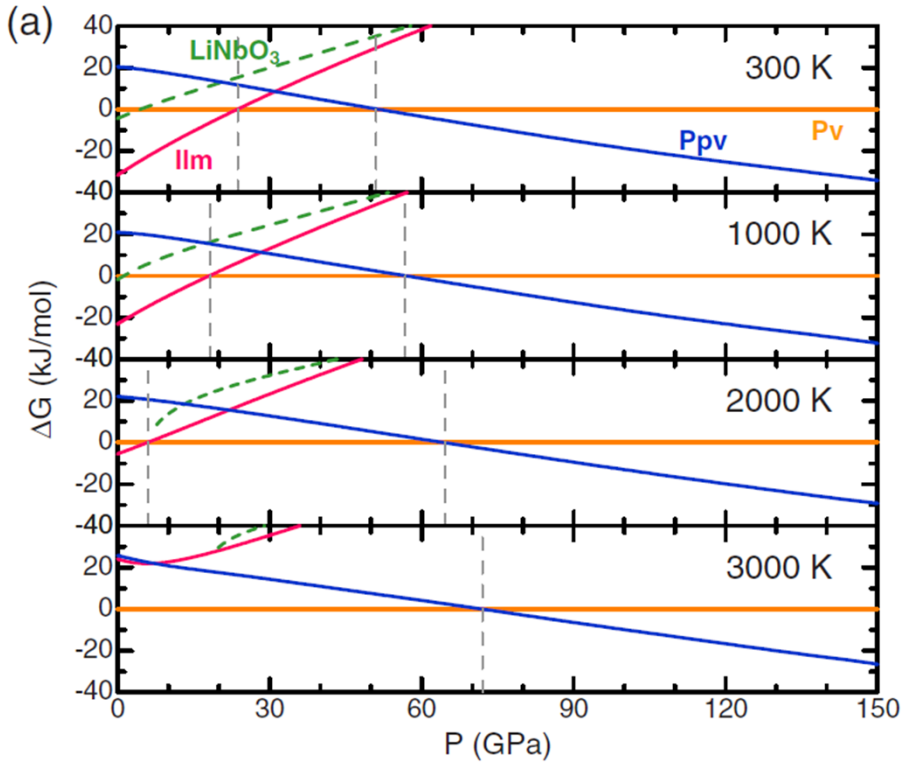


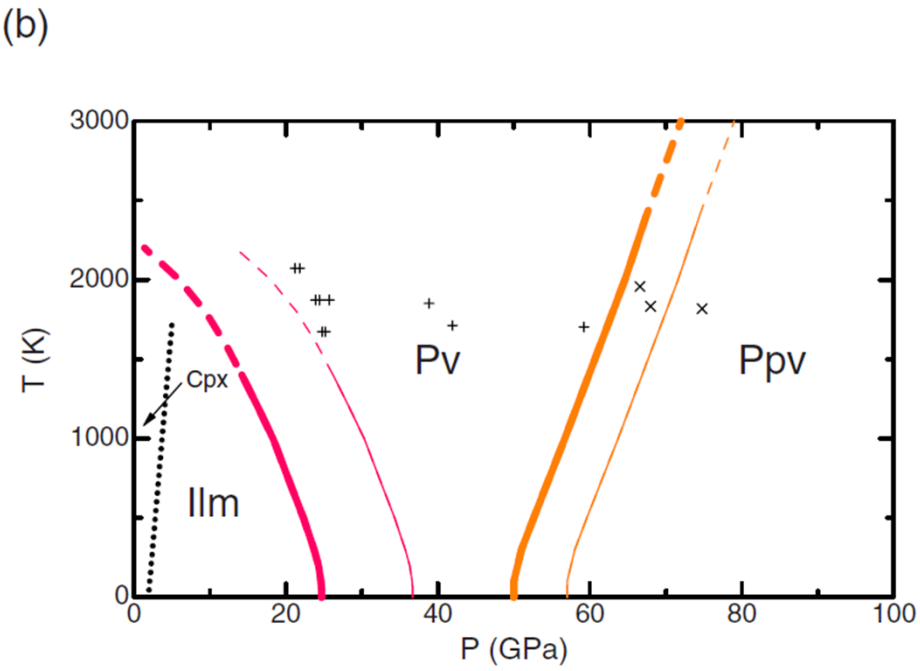
Knudson+ (2012) PRL

Thermodynamic phase stability

Gibbs free energy

$$G(P,T) = F(V,T) + P(V,T)V$$





$MgGeO_3$: Tsuchiya & Tsuchiya (2007) PRB

High-*P*,*T* phase boundaries can be determined.

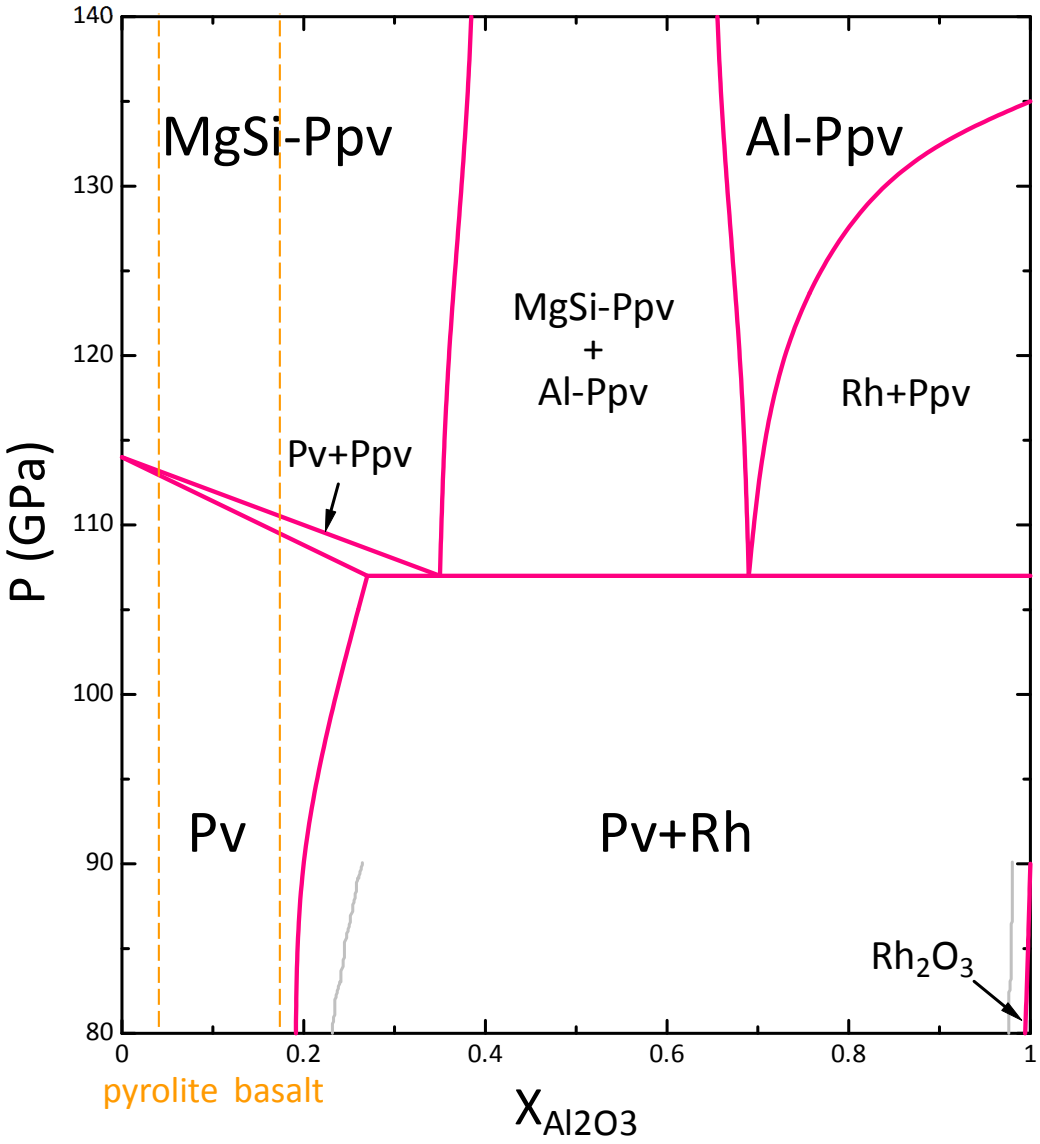
Multicomponent (P-V-T-x) phase equilibrium

PPv phase equilibrium in $MgSiO_3$-Al_2O_3 system

$$G(P,T,x) = -k_B T \ln Y(P,T,x)$$

$Y(P,T,x)$:
P,T partition function

Multi-configuration sampling (MCS) technique



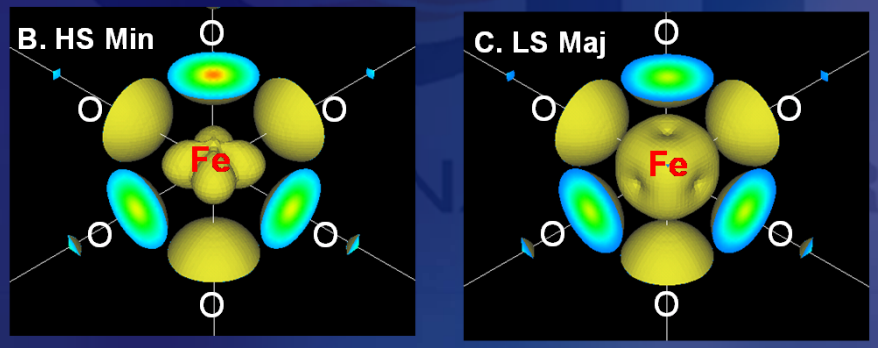
Tsuchiya & Tsuchiya (2008) PNAS

Internally consistent LDA+U for Fe-bearing system

$$E^{LDA+U}[n(\mathbf{r})] = E^{LDA}[n(\mathbf{r})] + E^{Hub}[\{n_m^{I\sigma}\}] - E^{DC}[\{n^{I\sigma}\}]$$

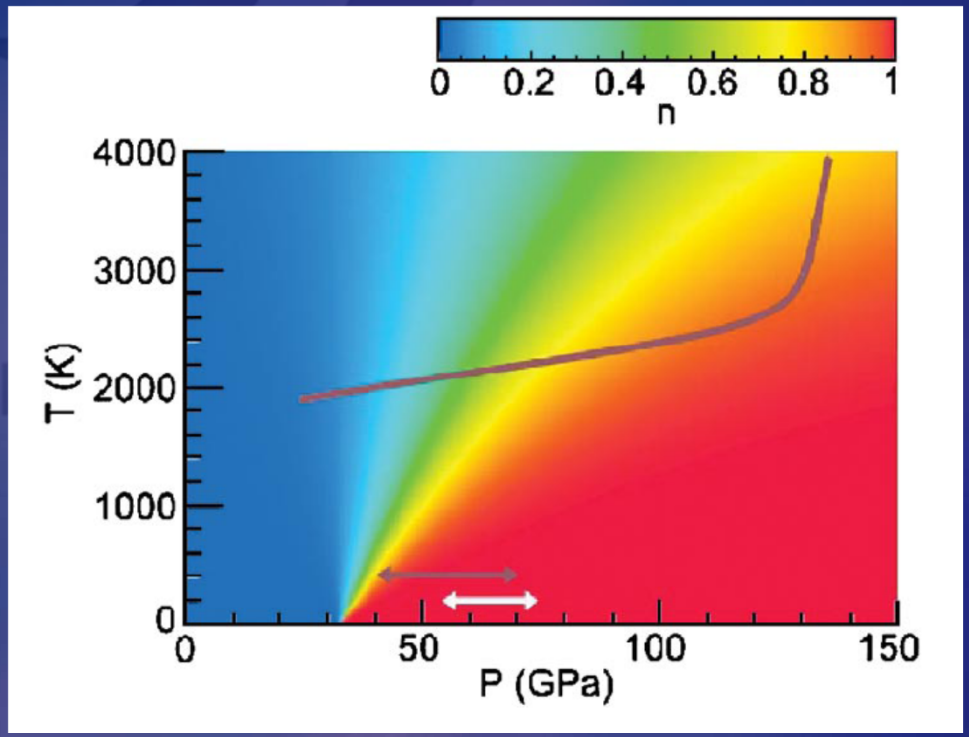
$$E^{Hub}[\{n_{mm'}^{I\sigma}\}] - E^{DC}[\{n^{I\sigma}\}] = \frac{U}{2}\sum_{I,\sigma} \mathrm{Tr}[\mathbf{n}^{I\sigma}(1-\mathbf{n}^{I\sigma})]$$

On-site Coulomb *U* parameter determined non-empirically based on a linear response formalism



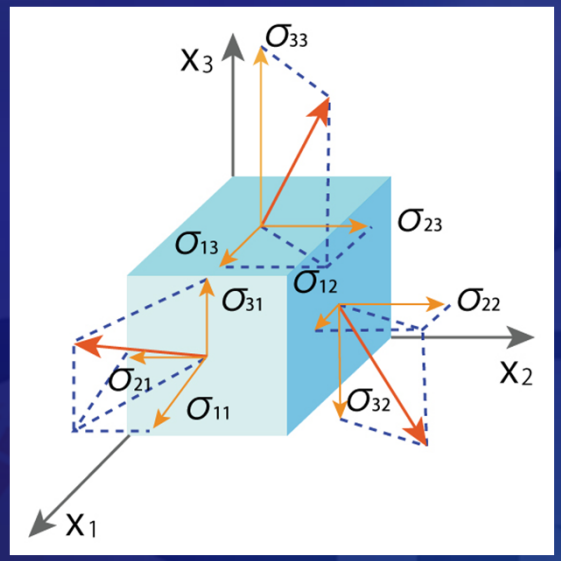
Tsuchiya+ (2006) PRL

Spin transition in ferropericlase (Mg,Fe)O



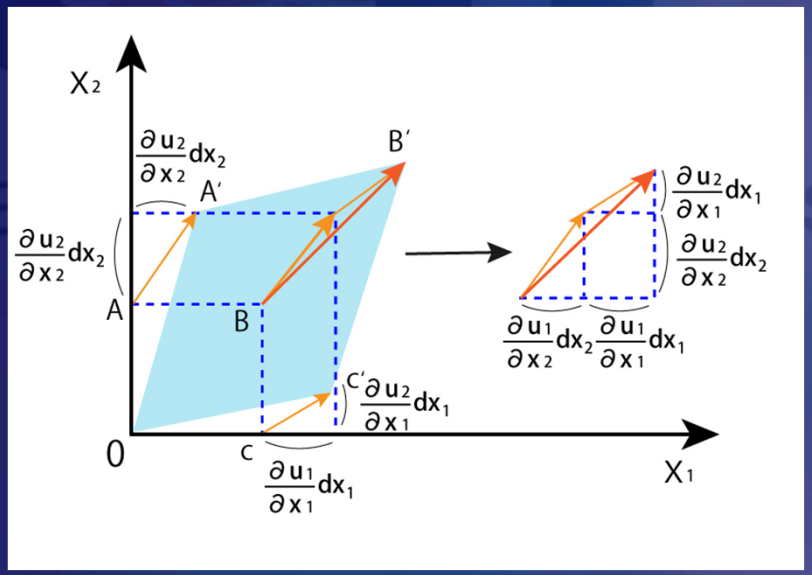
Crystal elasticity

Stress σ_{ij}



$$\sigma_{ij} = \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix}$$

Strain ε_{ij}



$$\varepsilon_{ij} = \begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33} \end{pmatrix}$$

$$\varepsilon_{ii} = \frac{\partial u_i}{\partial x_j}, \varepsilon_{ij} = \varepsilon_{ji} = \frac{1}{2}\left(\frac{\partial u_1}{\partial x_2} + \frac{\partial u_2}{\partial x_1}\right)$$

Elastic constant tensor

Linear response between stress and strain (Hooke's law)

$$\sigma_{ij} = \sum_{kl} c_{ijkl}\varepsilon_{kl} \quad \text{or} \quad \varepsilon_{ij} = \sum_{kl} s_{ijkl}\sigma_{kl}$$

c_{ijkl}: elastic stiffness tensor

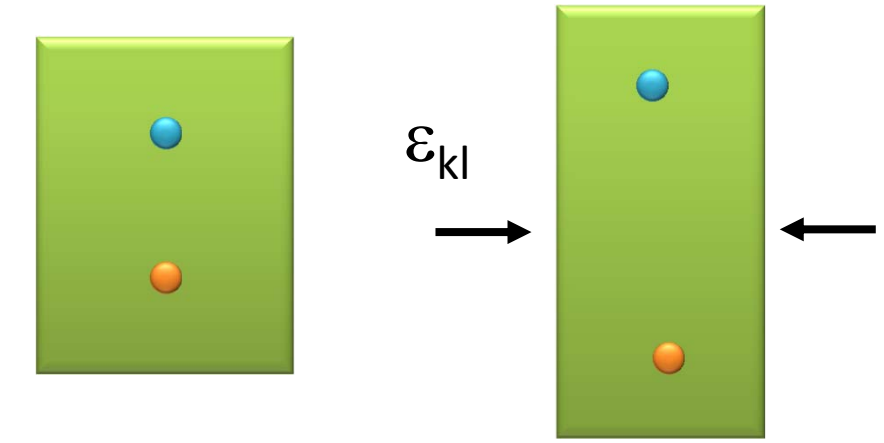
s_{ijkl}: elastic compliance tensor

$$(i, j, k, l = 1\sim3)$$

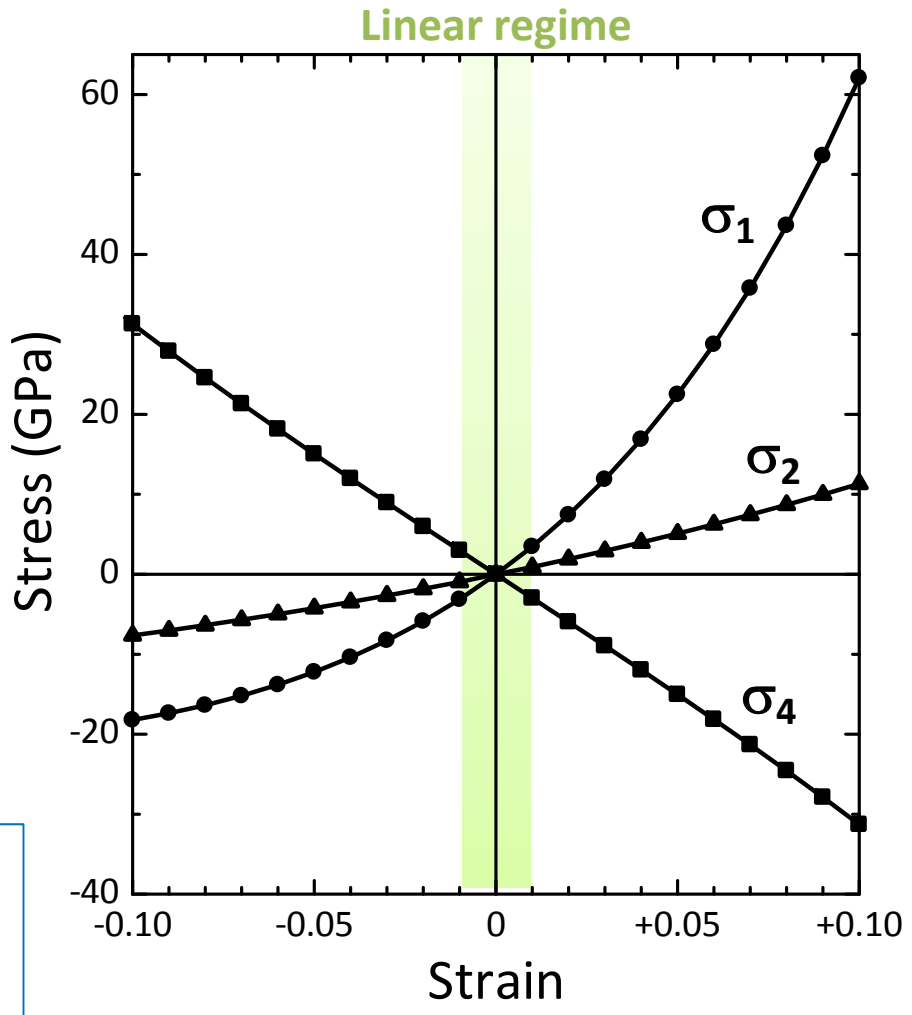
Voigt notation (simplified notation)

$$11 \to 1, 22 \to 2, 33 \to 3, 23 = 32 \to 4, 31 = 13 \to 5, 12 = 21 \to 6$$

$$\text{e.g.}, c_{1111} = c_{11}, \qquad c_{1122} = c_{12}, \qquad c_{2323} = c_{44}$$



MgO （P=0 GPa）



Linear regime typically within $|\varepsilon| \leq 0.01$

Tsuchiya & Kawai under review

Acoustic (elastic) wave speed

Equation of motion

$$\rho\frac{\partial^2 u_1}{\partial t^2}=\frac{\partial\sigma_{11}}{\partial x_1}+\frac{\partial\sigma_{12}}{\partial x_1}+\frac{\partial\sigma_{13}}{\partial x_1},$$
$$\rho\frac{\partial^2 u_2}{\partial t^2}=\frac{\partial\sigma_{22}}{\partial x_2}+\frac{\partial\sigma_{23}}{\partial x_2}+\frac{\partial\sigma_{21}}{\partial x_2},$$
$$\rho\frac{\partial^2 u_3}{\partial t^2}=\frac{\partial\sigma_{33}}{\partial x_3}+\frac{\partial\sigma_{31}}{\partial x_3}+\frac{\partial\sigma_{32}}{\partial x_3}$$

Orientational average

⇒ Polycrystalline wave speed

$$V_P=\sqrt{\frac{B_S+4/3\mu}{\rho}}\qquad V_S=\sqrt{\frac{\mu}{\rho}}\qquad V_\Phi=\sqrt{\frac{B_S}{\rho}}$$

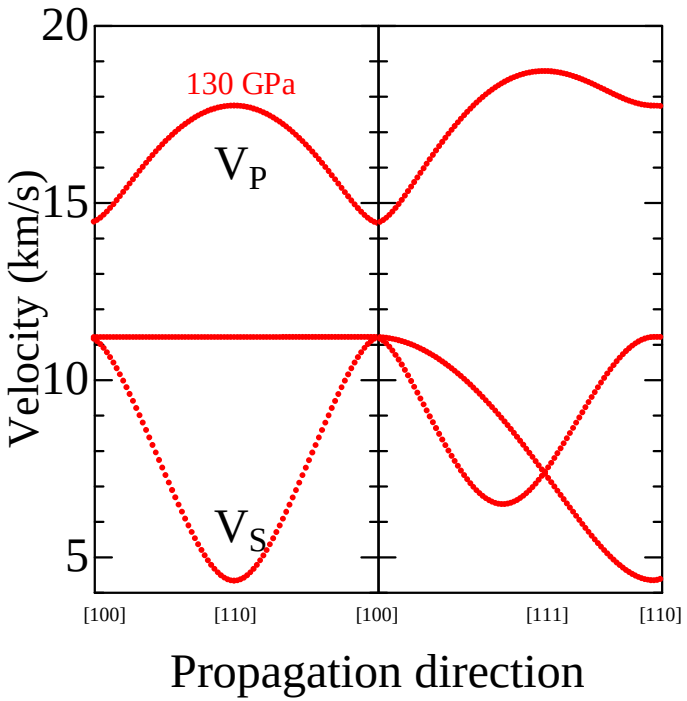
Direct comparison with seismological observations

Cristoffel's equation

$$\left|c_{ijkl}\mathbf{n}_j\mathbf{n}_l-\rho V\delta_{ik}\right|=0$$

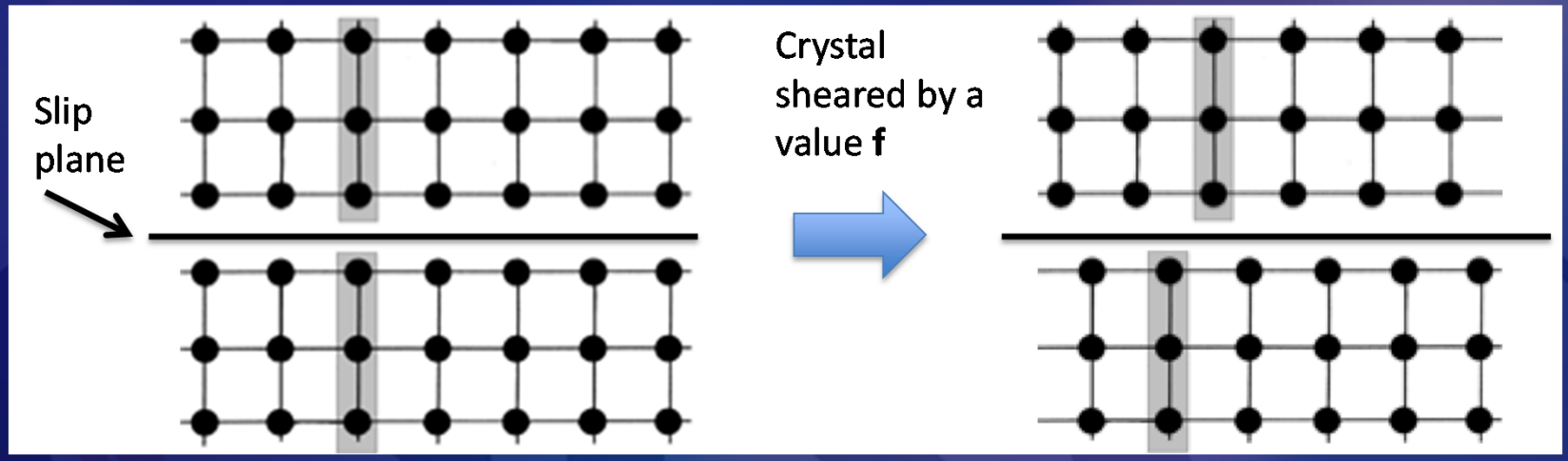
⇒Single-crystal wave speed

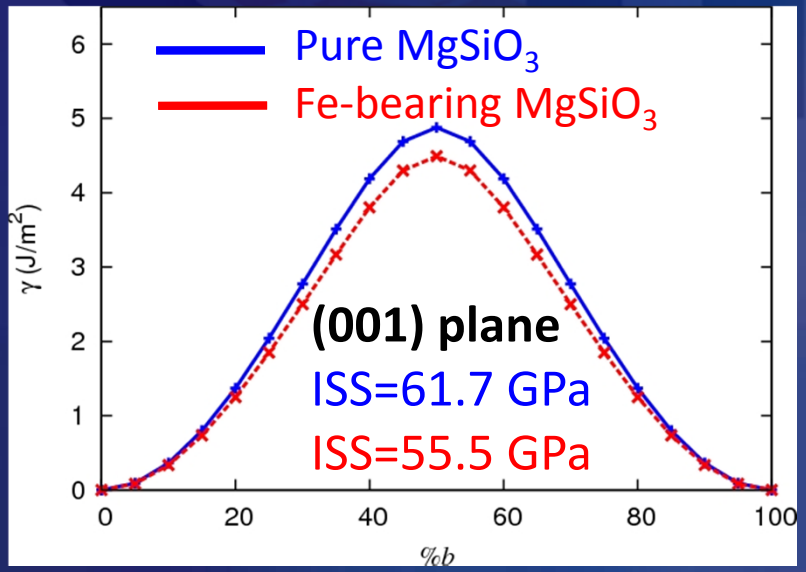
e.g., ice X phase (P=130 GPa)

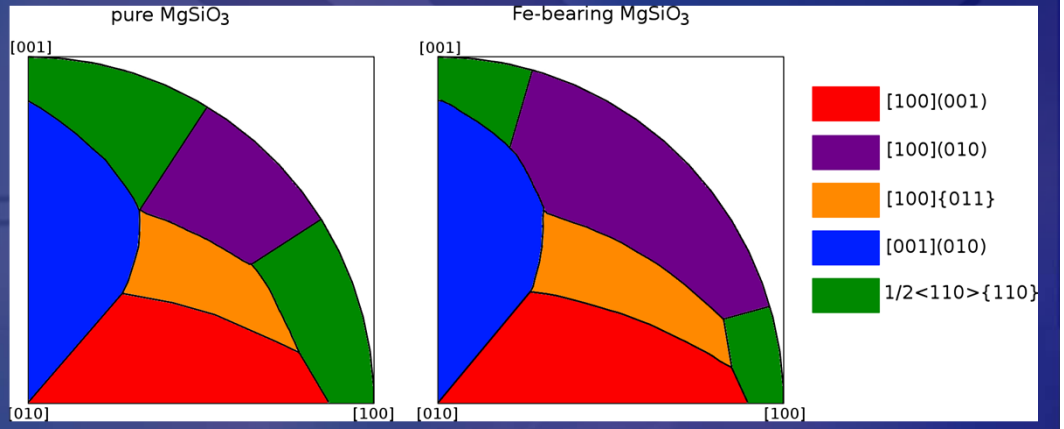


Shear response of crystals

Generalized Stacking Faults (GSF) Theory (*Vitek, 1968; Cordier+ 2004; etc*)







Metsue & Tsuchiya, under review

Solid viscosity still uneasy

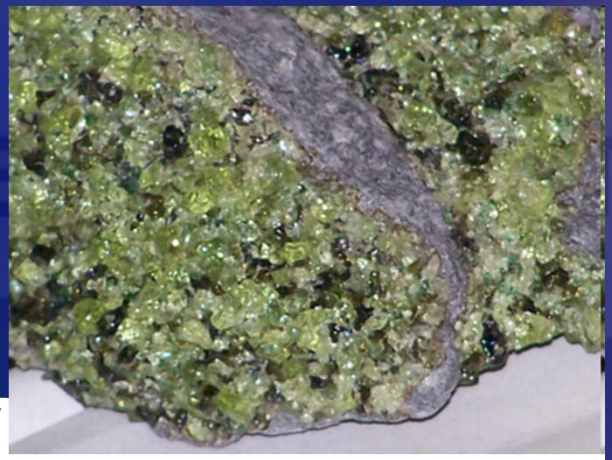
1. Fundamental methodologies of the ab initio electronic structure calculation method

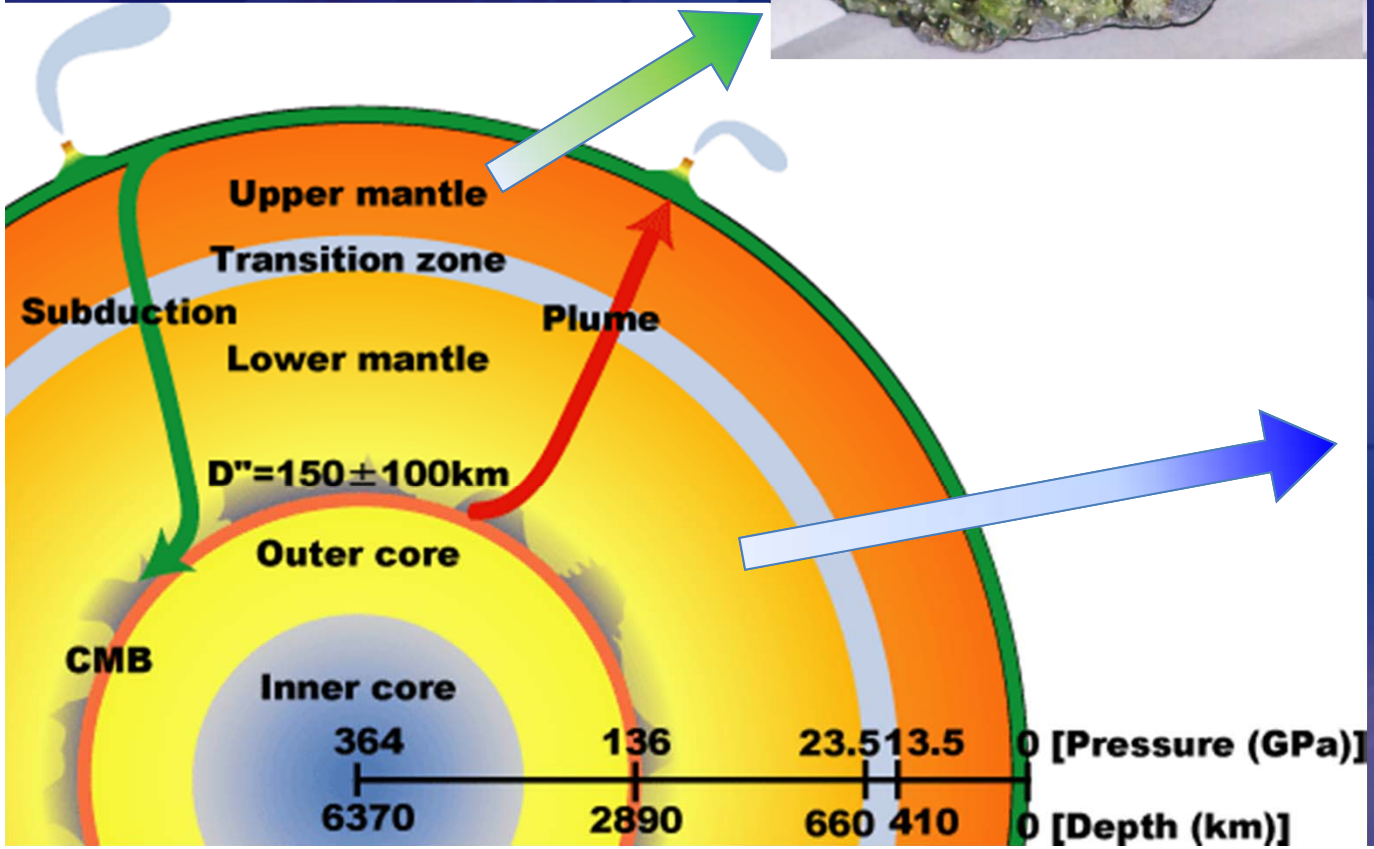
2. Applications to high-pressure mineral physics and Earth & planetary interiors

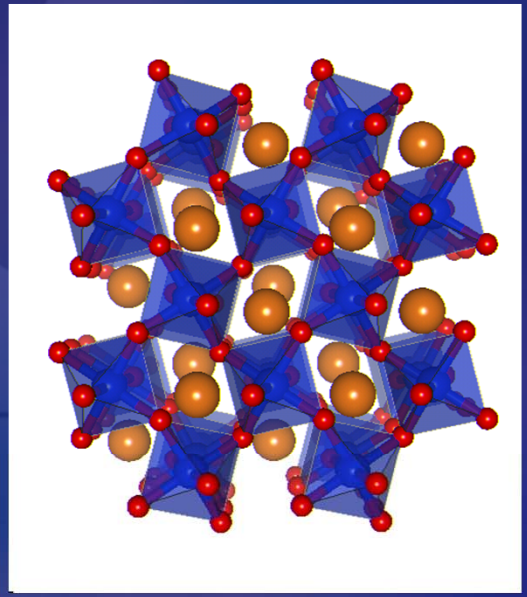
   - Phase relations including melting
   - Electronic property
   - Transport property

Example: Post-perovskite transition in $MgSiO_3$

Upper mantle:
Olivine Mg_2SiO_4

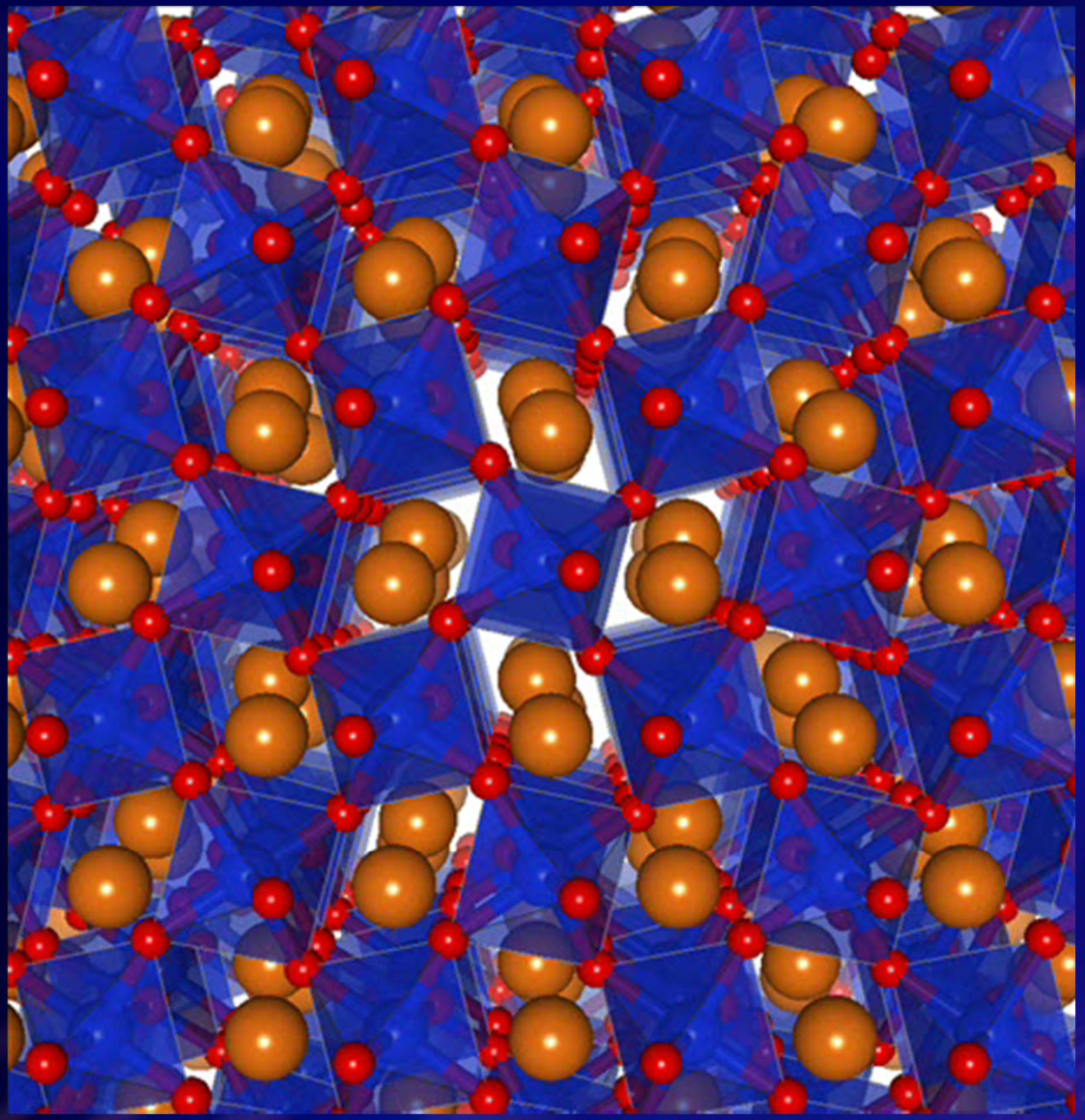






Lower mantle:
Perovskite $MgSiO_3$

Perovskite to post-perovskite structural change

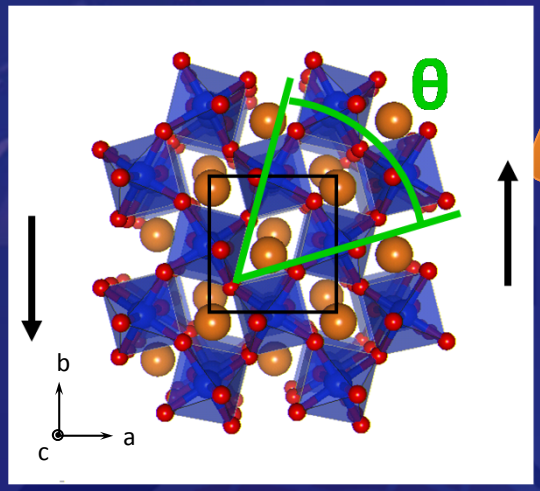


Mg

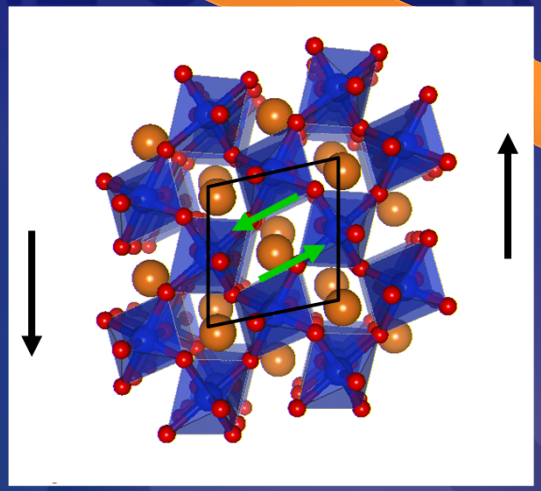
Si

O

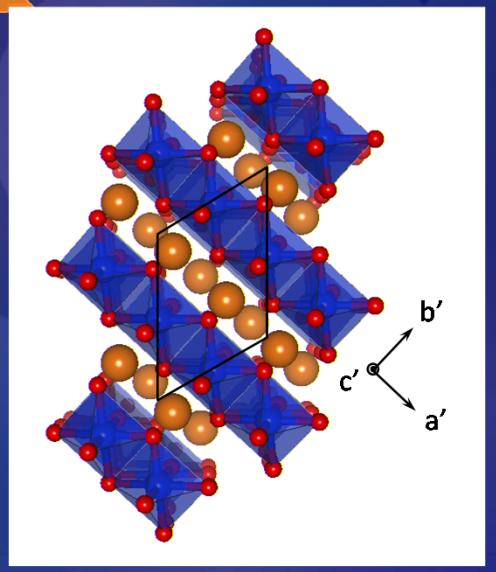
Tsuchiya+ (2004) EPSL



Perovskite (Lower mantle)



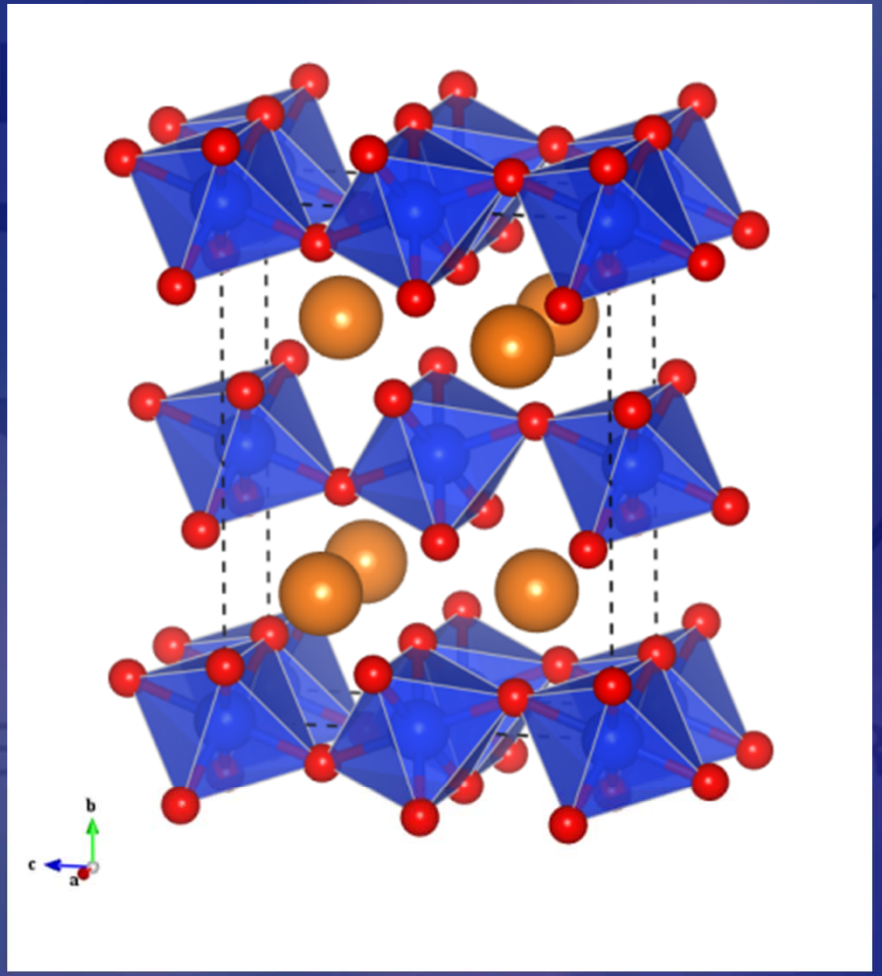
Shear deformation (ε_6)



Post-Perovskite (D" layer)

$CaIrO_3$-type structure

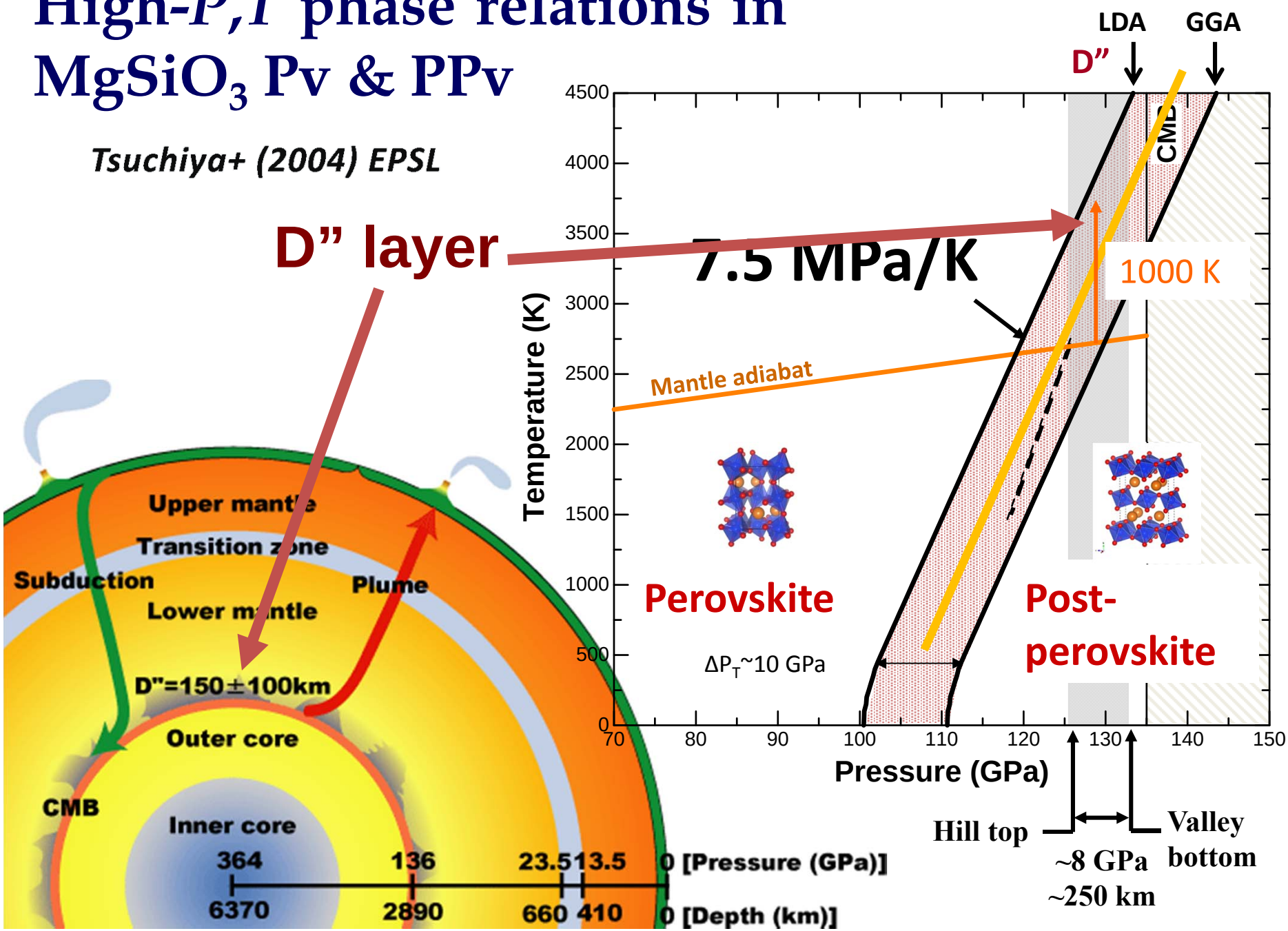
- Orthorhombic cell ($Cmcm, Z = 4$) with SiO_6 octahedra.
- Those octahedra are connected with each other by sharing edges along the **a** direction. This is a major reason for the structure more stable than Pv.



Exper: Murakami+ (2004)
Theor: Tsuchiya+ (2004)
etc

High-*P*,*T* phase relations in $MgSiO_3$ Pv & PPv

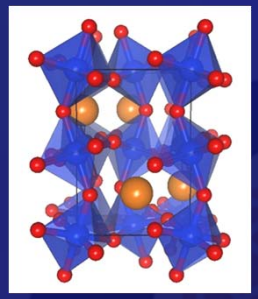
Tsuchiya+ (2004) EPSL

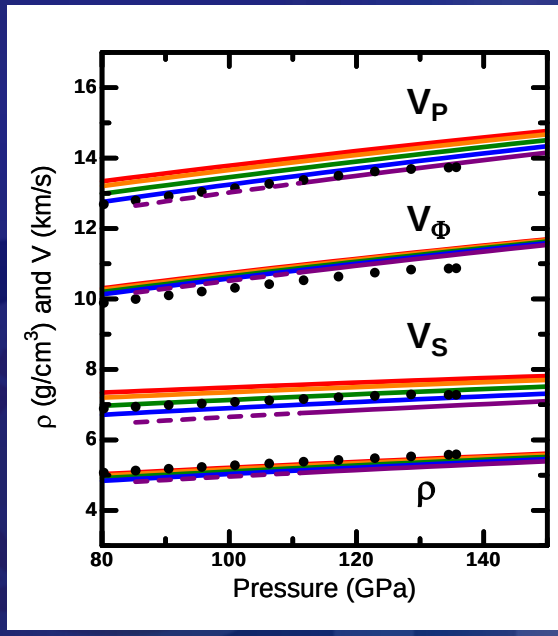


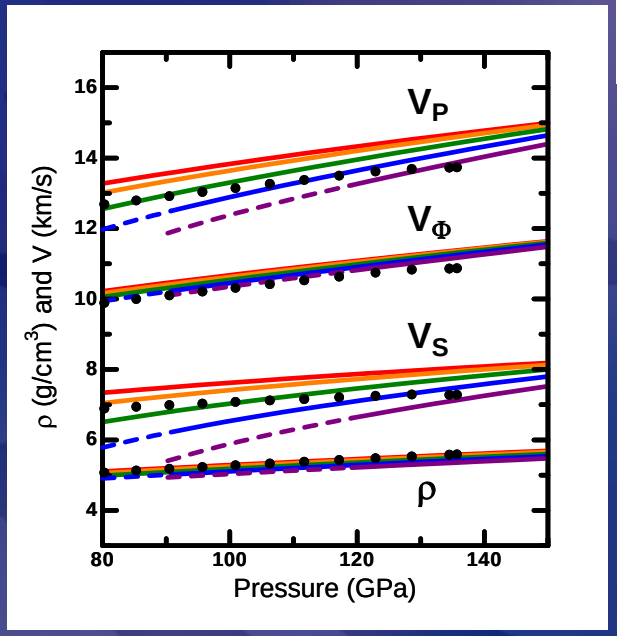
High-*P,T* elastic wave velocities and density of $MgSiO_3$-Pv and PPv

300 K
1000 K
2000 K
3000 K
4000 K

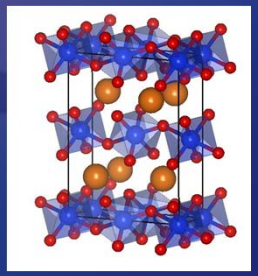
Pv







PPv



Wentzcovitch, Tsuchiya & Tsuchiya (2006) PNAS

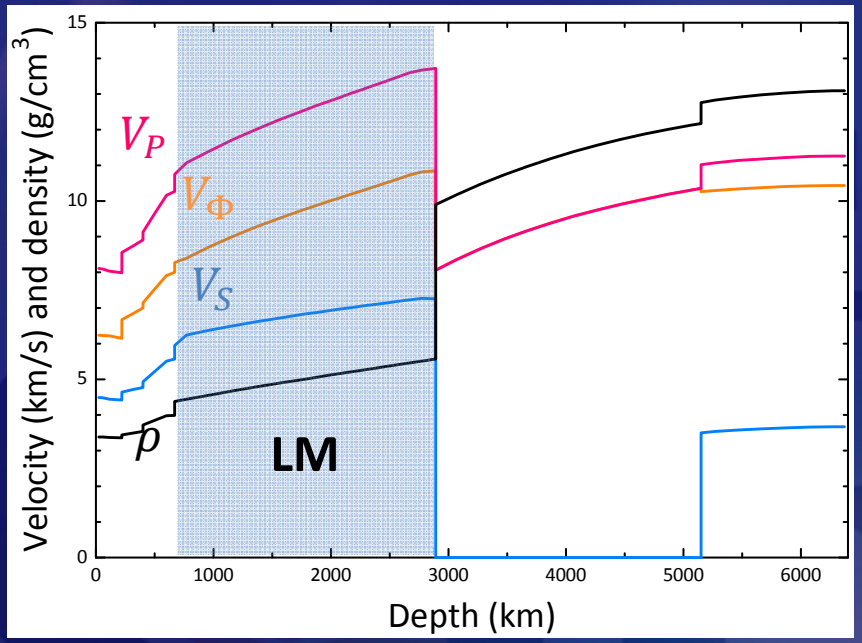
Effects of Fe and Al incorporation

Table 2. Logarithmic Derivatives of Velocities and Density With Respect to Lateral Variations in the Fe and Al Content at 100 GPa

	$\partial \ln V_P/\partial X$		$\partial \ln V_S/\partial X$		$\partial \ln V_\Phi/\partial X$		$\partial \ln \rho/\partial X$	
	Fe	Al	Fe	Al	Fe	Al	Fe	Al
pv	−0.140	−0.049	−0.220	−0.083	−0.098	−0.026	0.231	0.017
ppv	−0.156	−0.057	−0.236	−0.131	−0.099	−0.012	0.228	0.021

Tsuchiya & Tsuchiya (2006) GRL

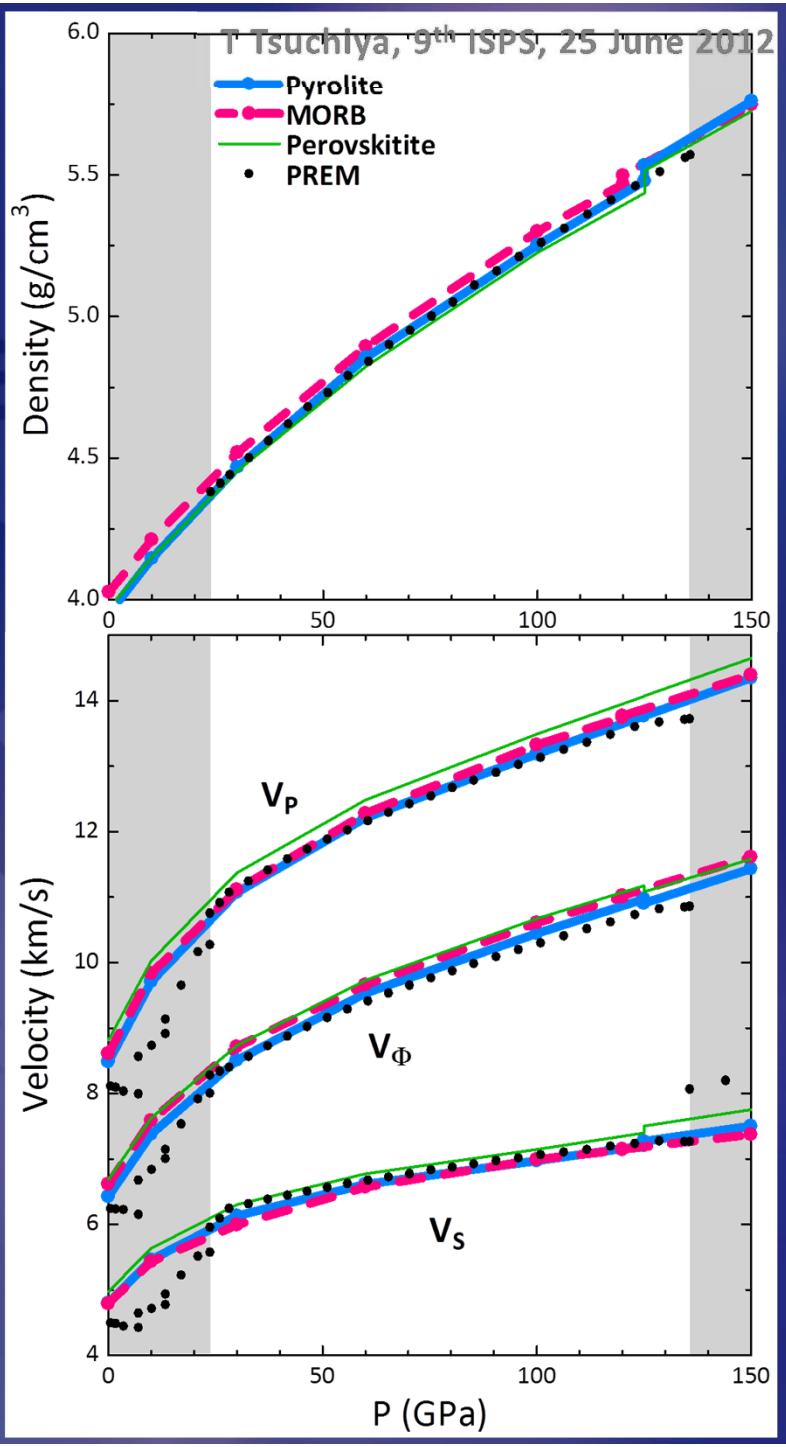
Velocity structure of the Earth



Observations (PREM, ***Dziewonski & Anderson, 1981)***

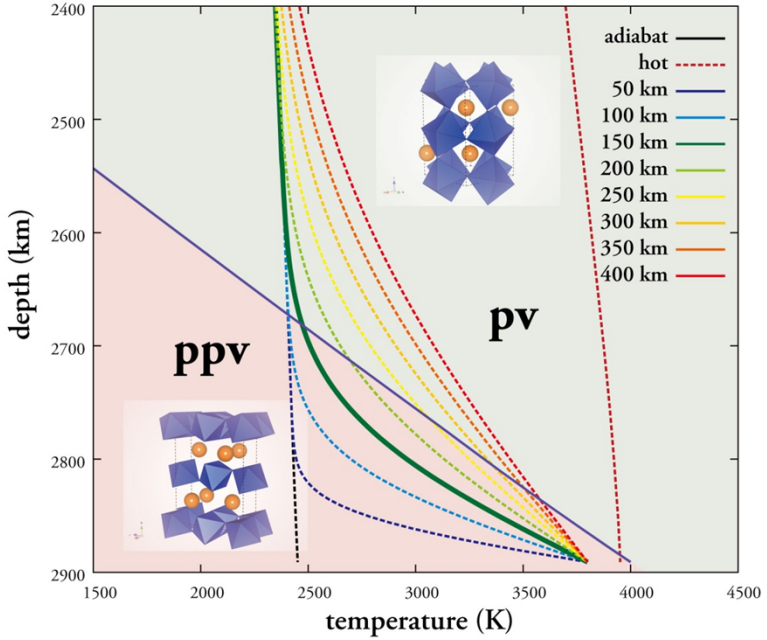
Calculated velocities and density of some model rocks along adiabatic geotherm
(Tsuchiya PEPI 2011;
Tsuchiya & Kawai, under review)

V_S is the most insensitive to the composition among these three models.
(cf, Murakami+ 2012)



D" velocity structure model

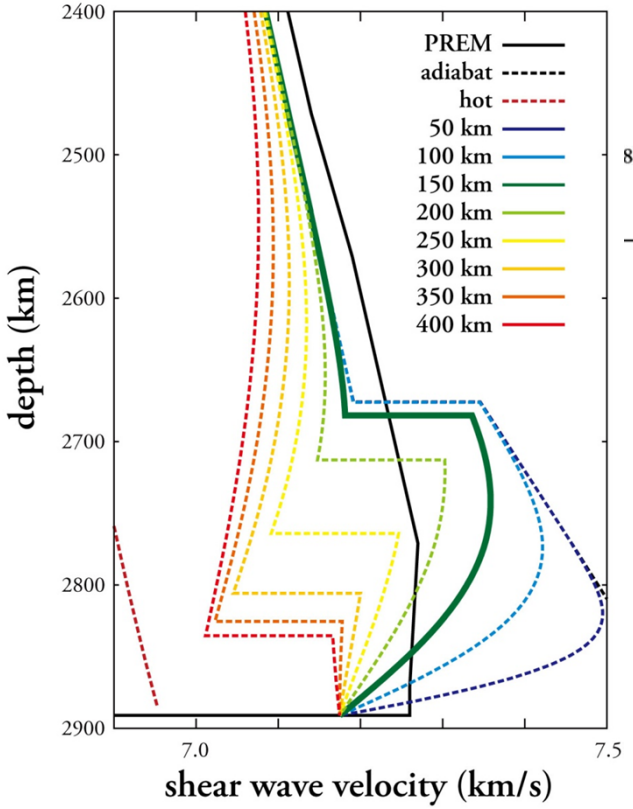
Case: T_{CMB} = 3800 K



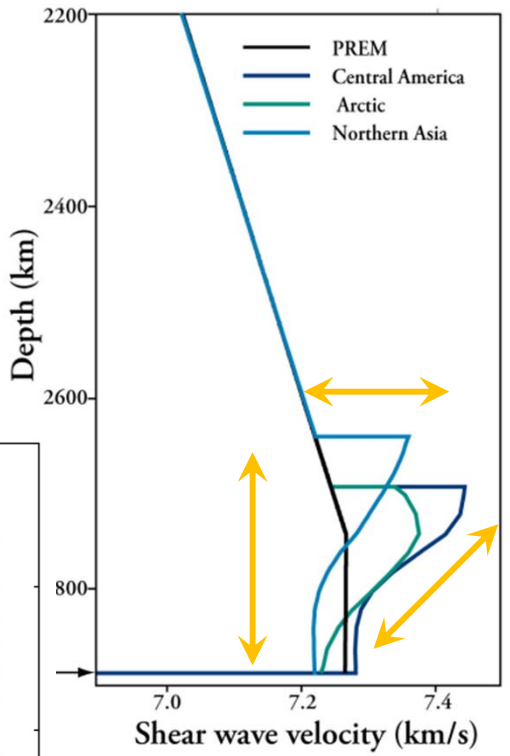
Temperature structure

ΔT_{TBL} = 1200~1300 K

D_{TBL} = 250 km



Modeled velocity structure



Observations

Kawai & Tsuchiya (2009) PNAS

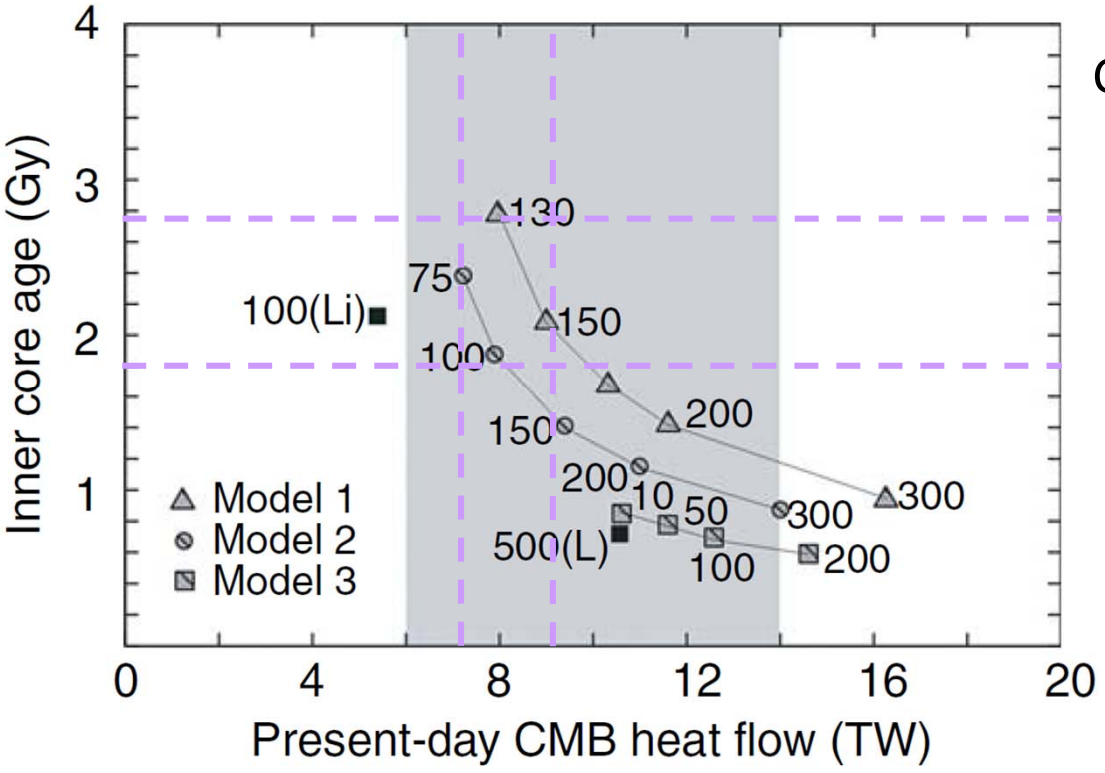
About CMB heat flux

CMB heat flux $q \sim \kappa \frac{\Delta T_{TBL}}{D_{TBL}}$

ΔT_{TBL} = 1200~1300 K
D_{TBL} = 250 km
κ = ~10 W K^{-1}m^{-1} ← Representative value

} ***Kawai & Tsuchiya (2009)***

= **7~9 TW**

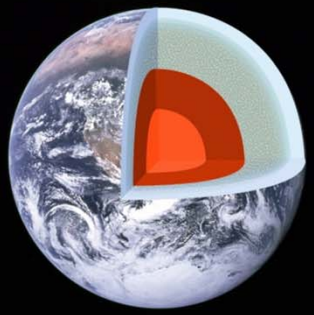


Relationship btwn
CMB heat flow and Inner core age
(Nimmo, ToG, 2007)

Estimated inner core age
= 2~3 Gy

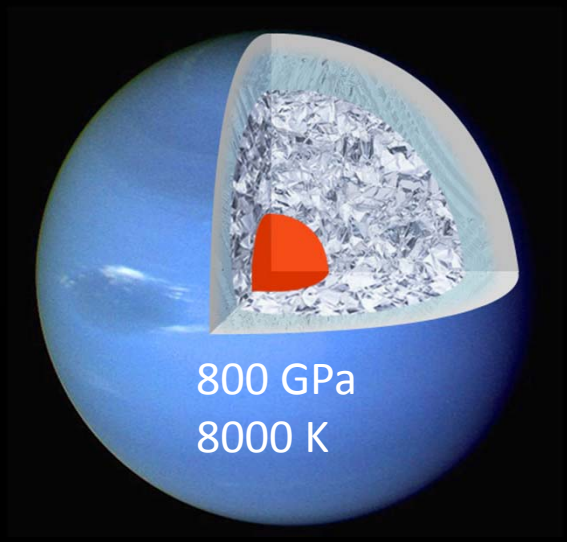
However, ***κ* (thermal conductivity)** of minerals under pressure still highly unclear

Extend to planetary interiors



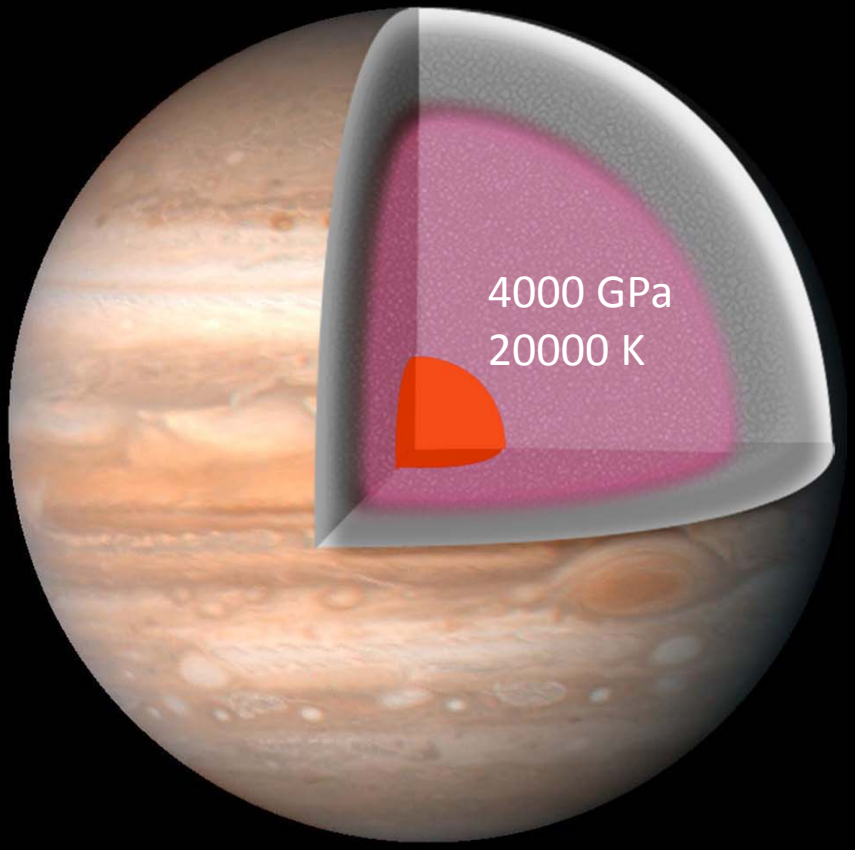
360GPa
6000 K

Rocky (silicate) mantle +
iron core



Icy (H_2O,CH_4 + rocky core)

~2$M_\oplus$



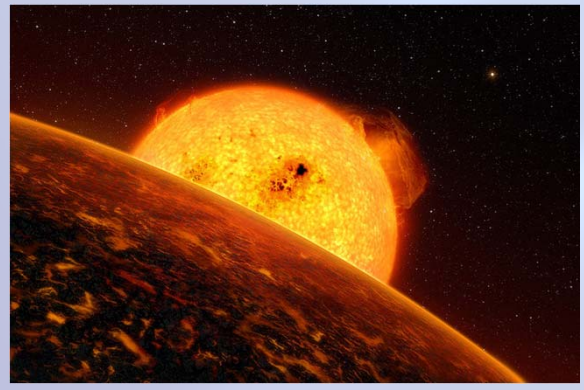
Gassy (H,He + rock+ice core?)

~10$M_\oplus$

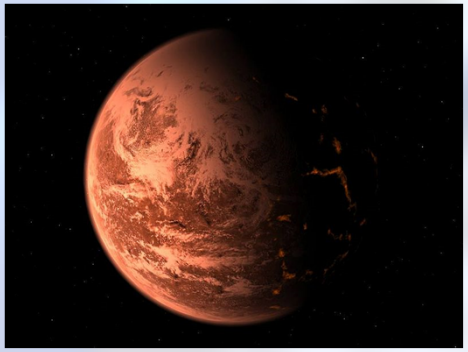
e.g., Guillot (1999) Science

Now, more than 700 exoplanets have been found.

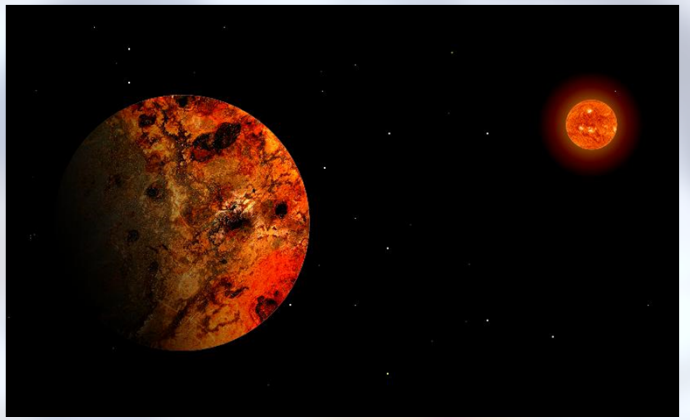
Some of them are terrestrial = **Super-Earths (SE).**



CoRoT-7b (~4.8$M_\oplus$)

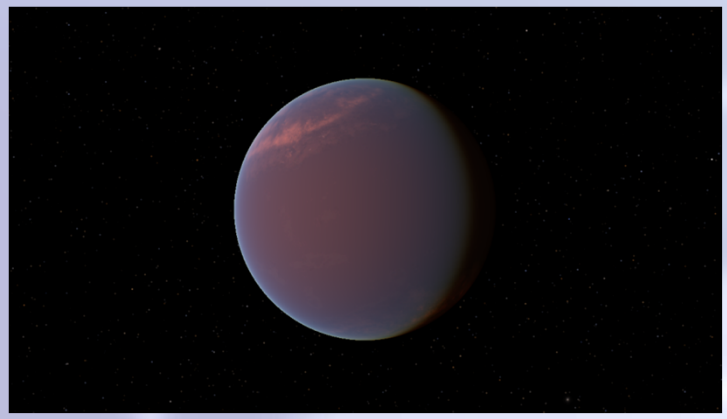


GJ876d (~7.5$M_\oplus$)

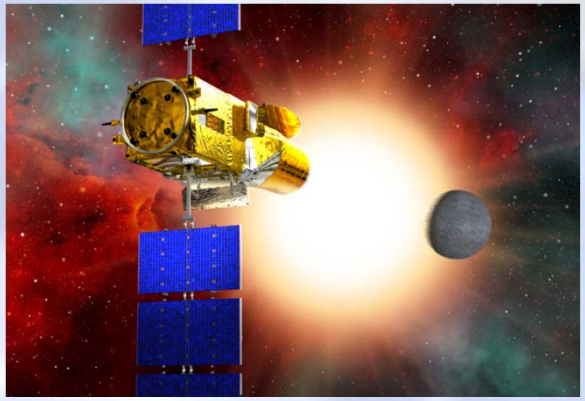


HD69830b (~10$M_\oplus$)

http://exoplanet.eu/



GJ1214 (~6.55$M_\oplus$ rock+H_2O)

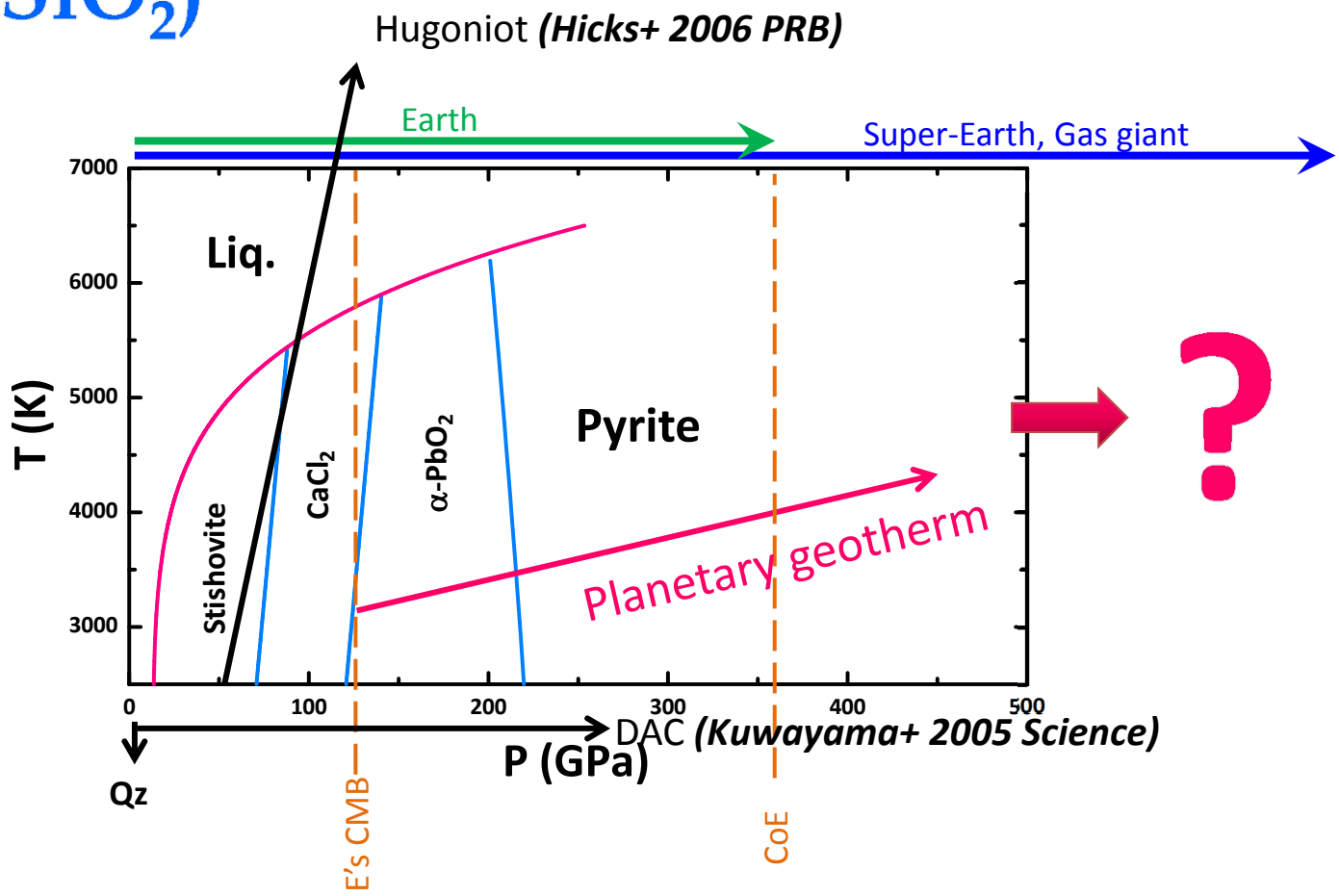


CoRoT space telescope (France)

Kepler space telescope (USA)

Rivera+ (2005); Udry+ (2007); Charbonneau+ (2009); Barnes+ (2010); etc

High-*P*,*T* phase relation of Earth materials (ex. SiO_2)

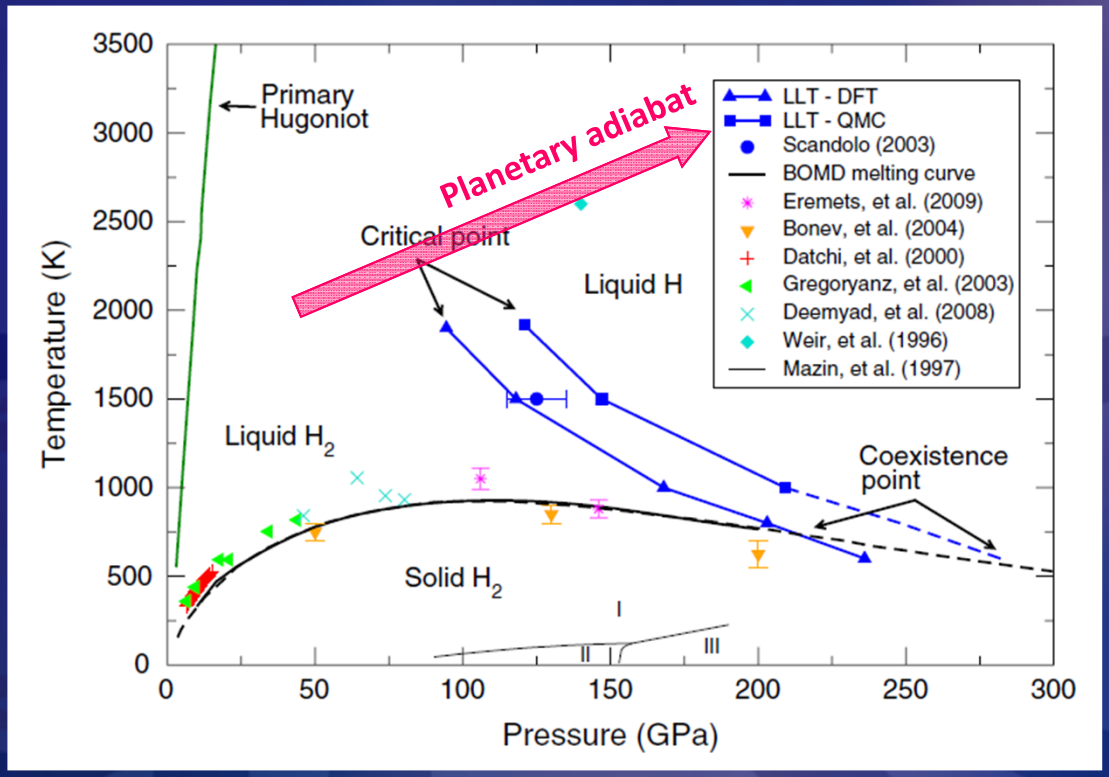


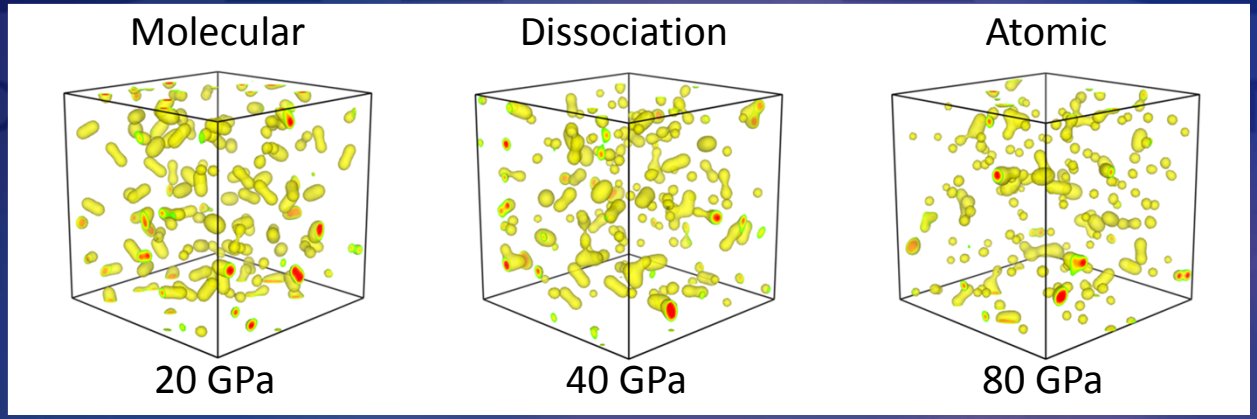
- High-*P*,*T* phase relations highly unclear at ultrahigh pressures
- But several important advances made by ab initio calculations

Hydrogen

Morales+ (2010) PNAS

Ab initio MD

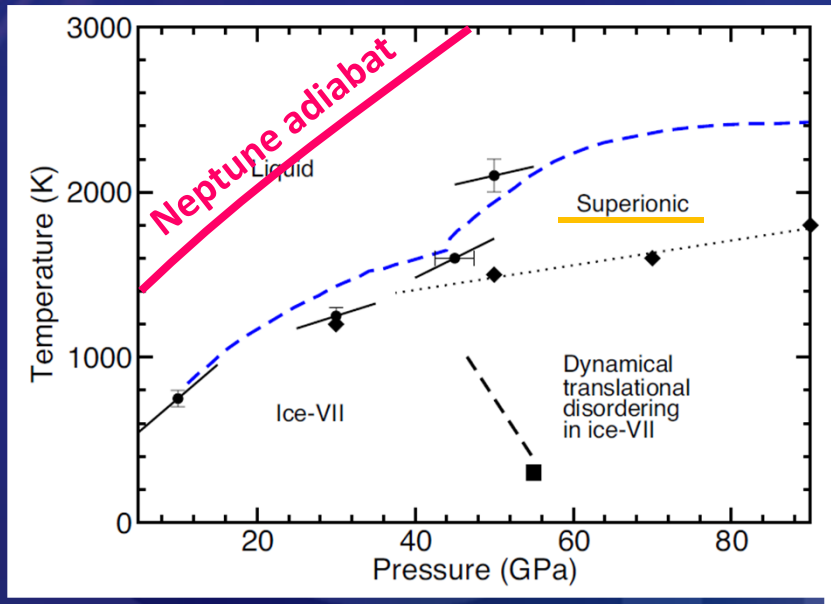




Water

Schwegler+ (2008) PNAS

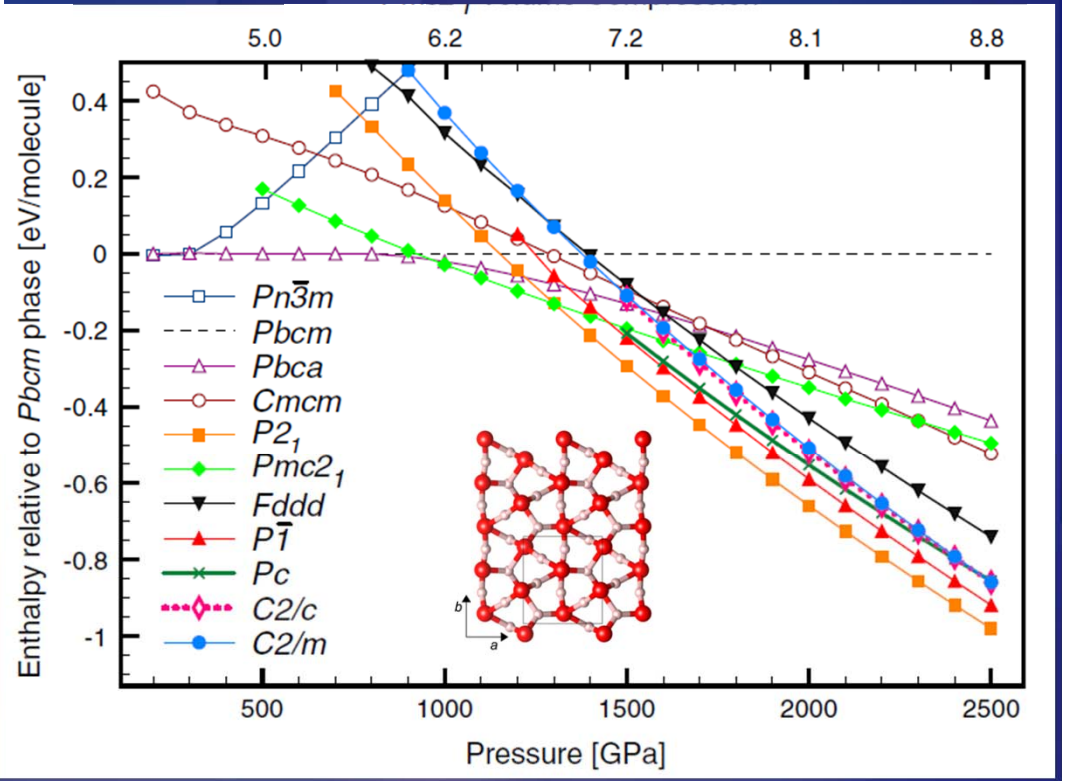
Ab initio melting curve



Ice

Hermann+ (2012) PNAS

Ab initio static phase stability

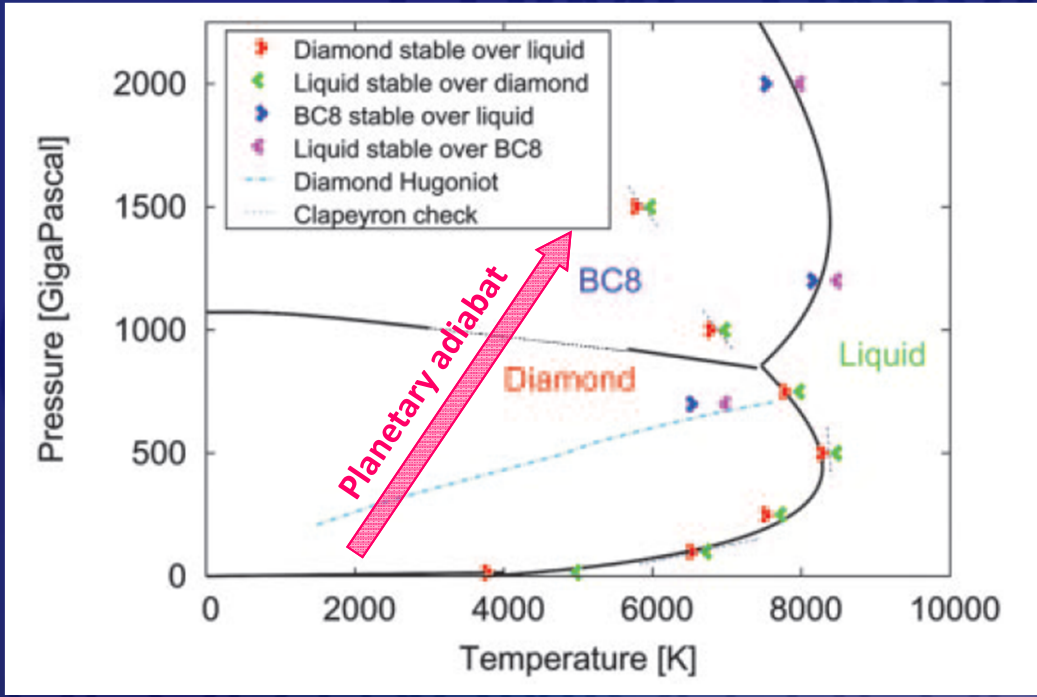


Carbon

"Diamonds in the sky" Ross+ (1981) Nature ?

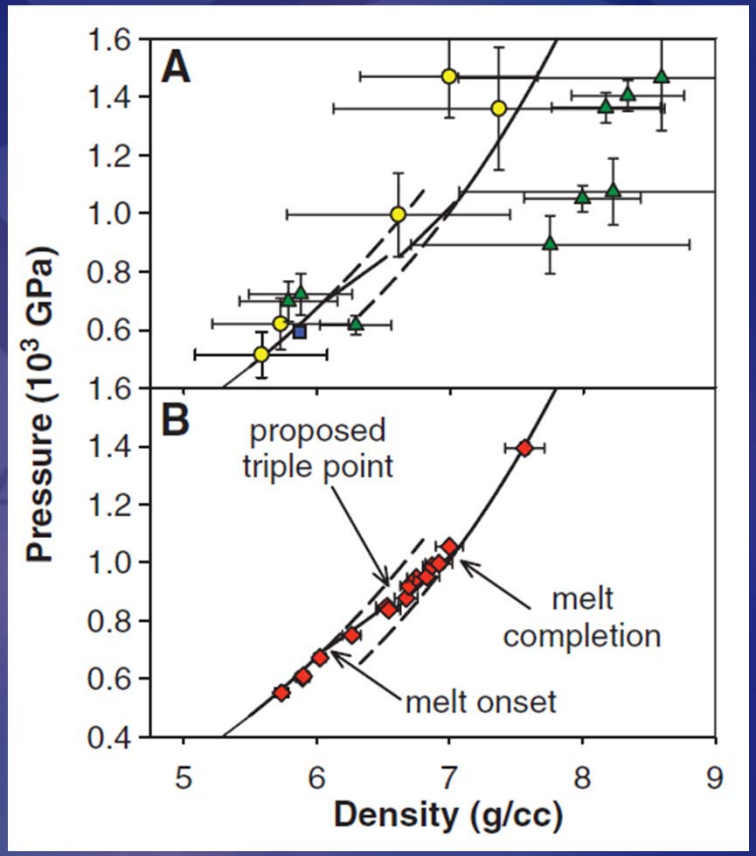
Correa+ (2006) PNAS

Ab initio high-*P*,*T* phase diagram of C



Knudson+ (2008) Science

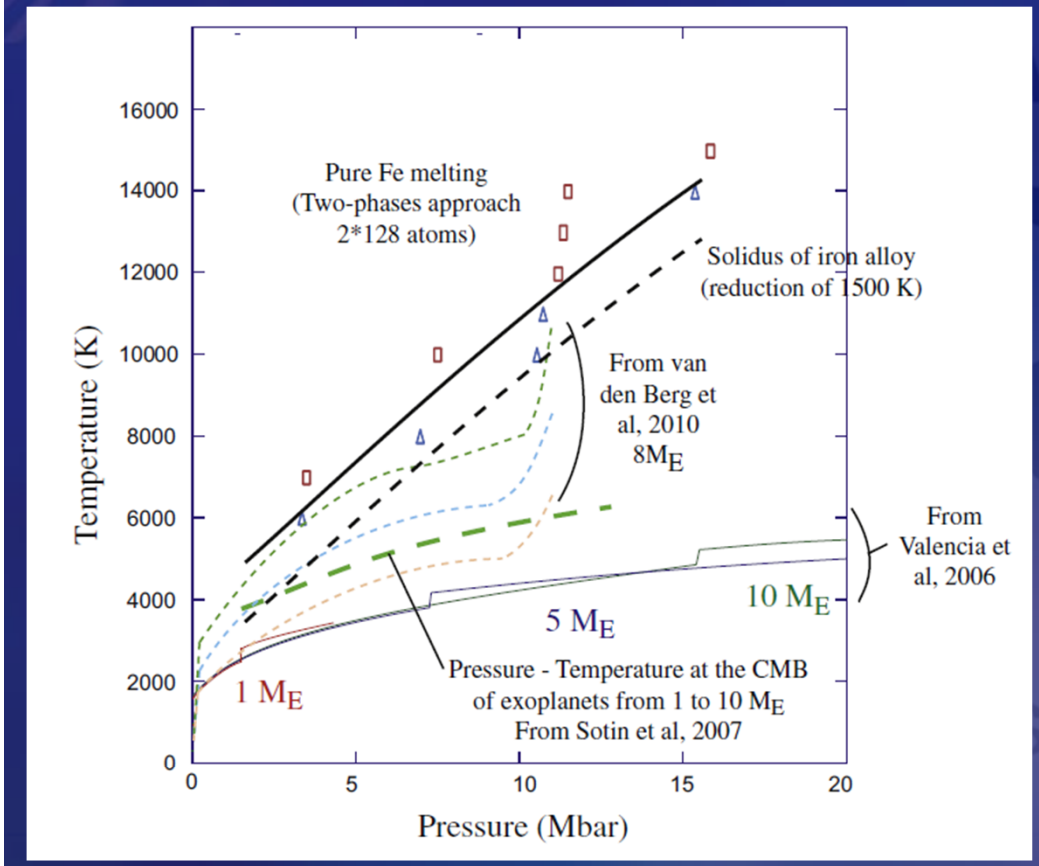
Experimental confirmation of the Dia-BC8-Liq triple point



Iron

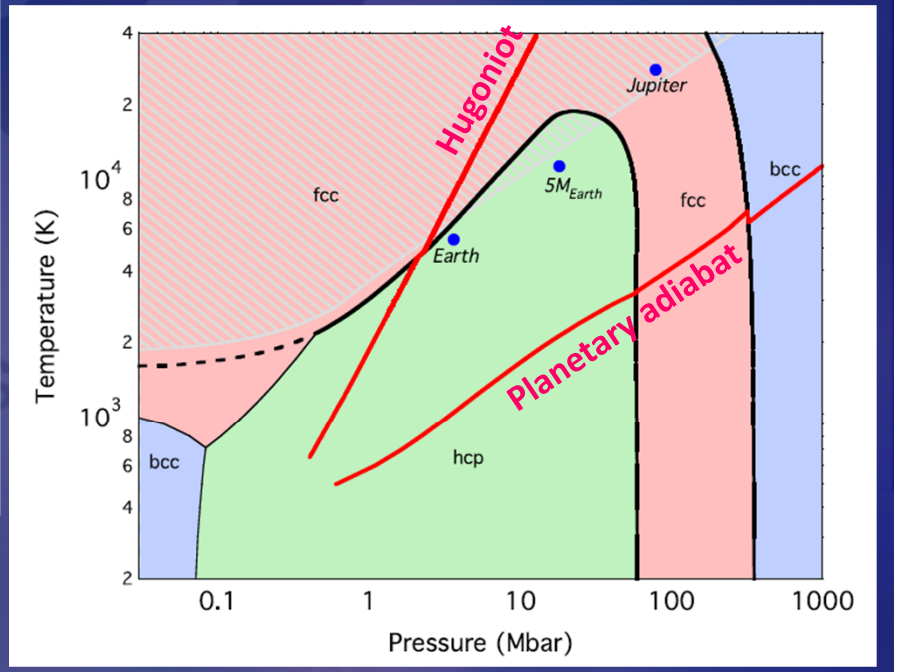
Morard+ (2011) HEDP

Ab initio melting curve



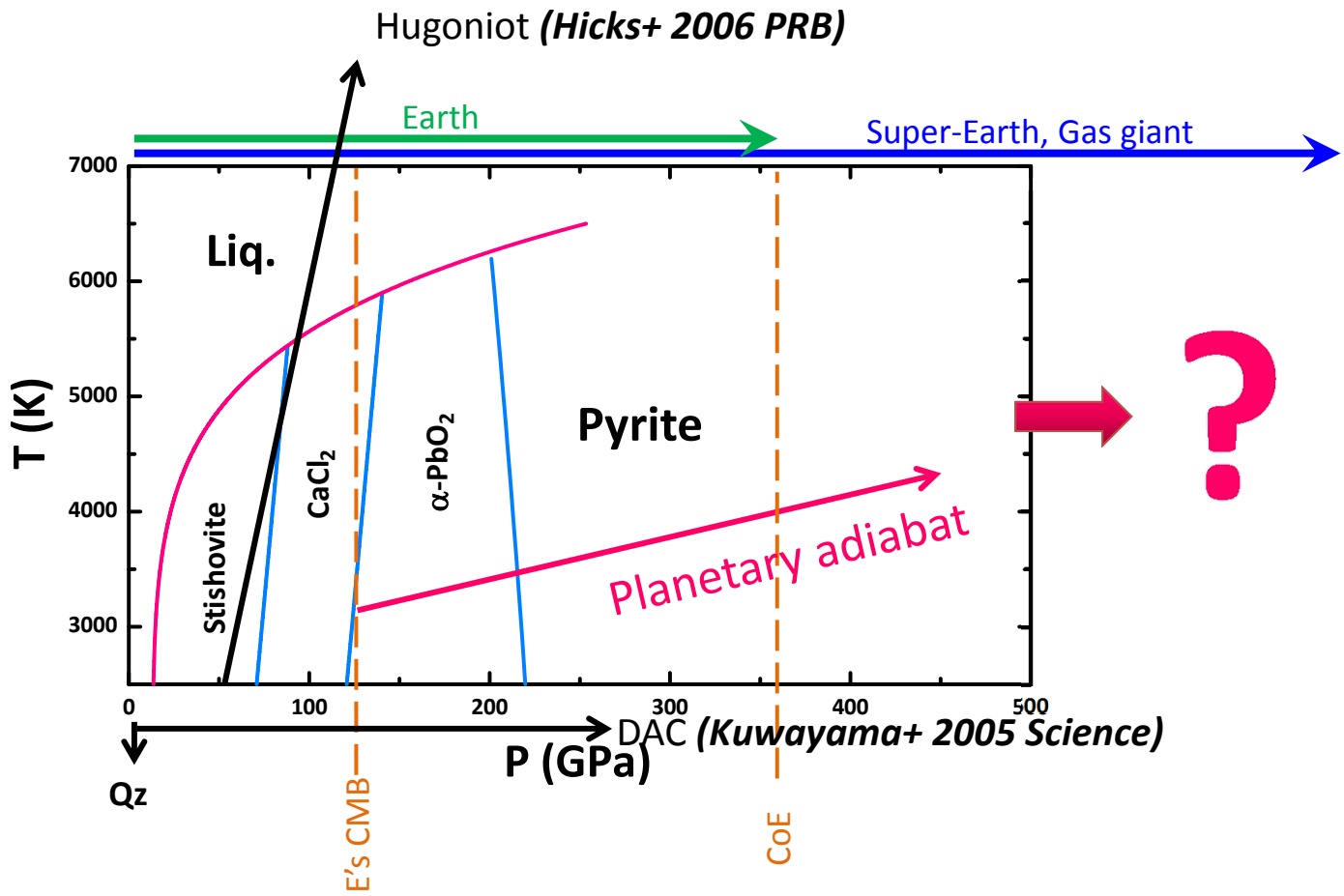
Stixrude (2012) PRL

Ab initio High-*P*,*T* phase diagram



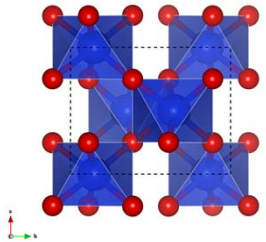
No liquid iron core in giant planets

High-P,T phase relation of SiO_2

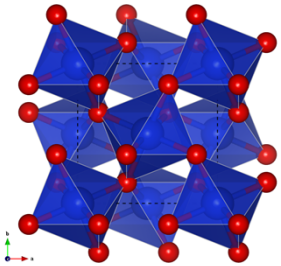


Dense packing structures with AX_2 stoichiometry for initial models (15 in total)

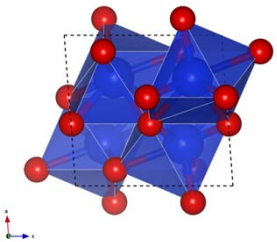
(1) α-PbO_2 (VI)



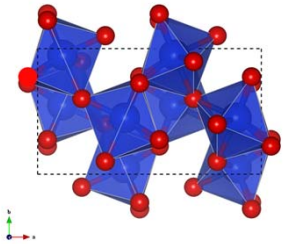
(2) Pyrite (FeS_2) (VI)



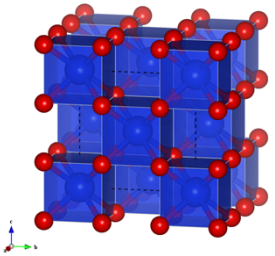
(3) Baddeleyite (VII) (ZrO_2)



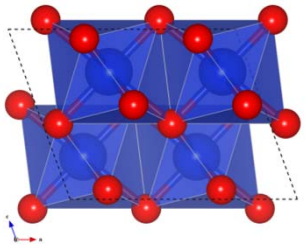
(4) Orthorhombic-I (VII)



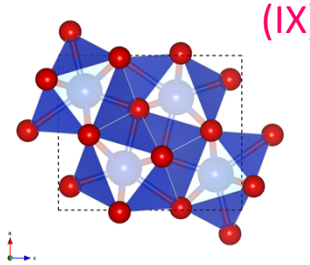
(5) Fluorite (CaF_2) (VIII)



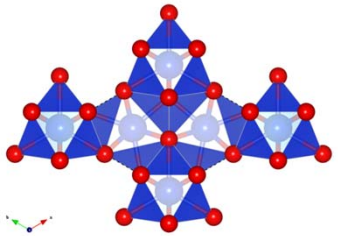
(6) $P2_1/m$ (VIII)



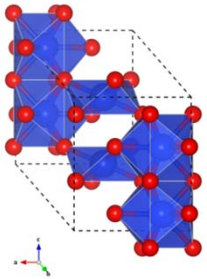
(7) Cotunnite ($PbCl_2$) (IX)



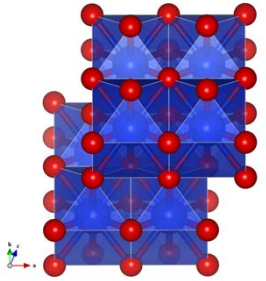
(8) Fe_2P (IX)



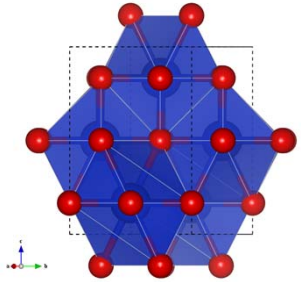
(9) P-1 (IX)



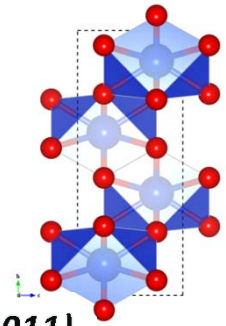
(10) $MoSi_2$ (X)



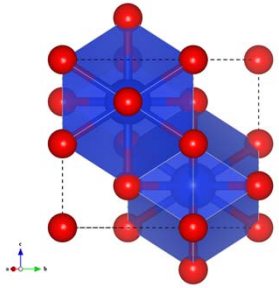
(11) $CrSi_2$ (X)



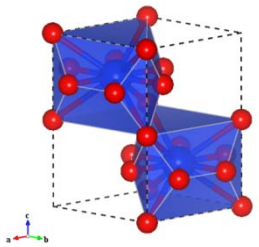
(12) Cmcm (X)



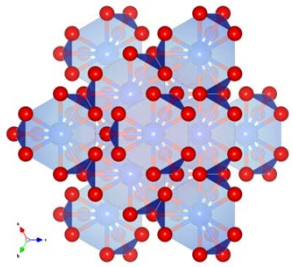
(13) Ni_2In (XI)



(14) $MgZn_2$ (XII)



(15) $MgCu_2$ (XII)



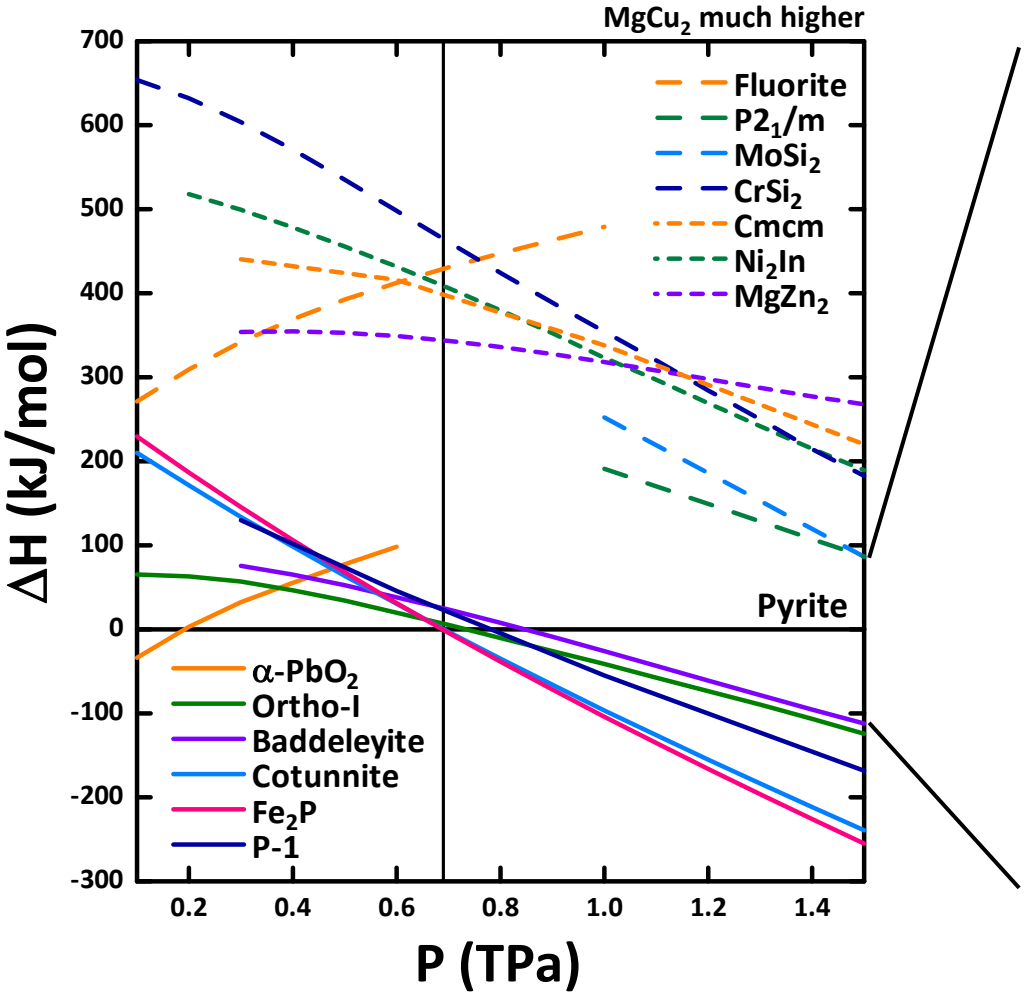
Blue: Si

Red: O

Tsuchiya & Tsuchiya (2011)

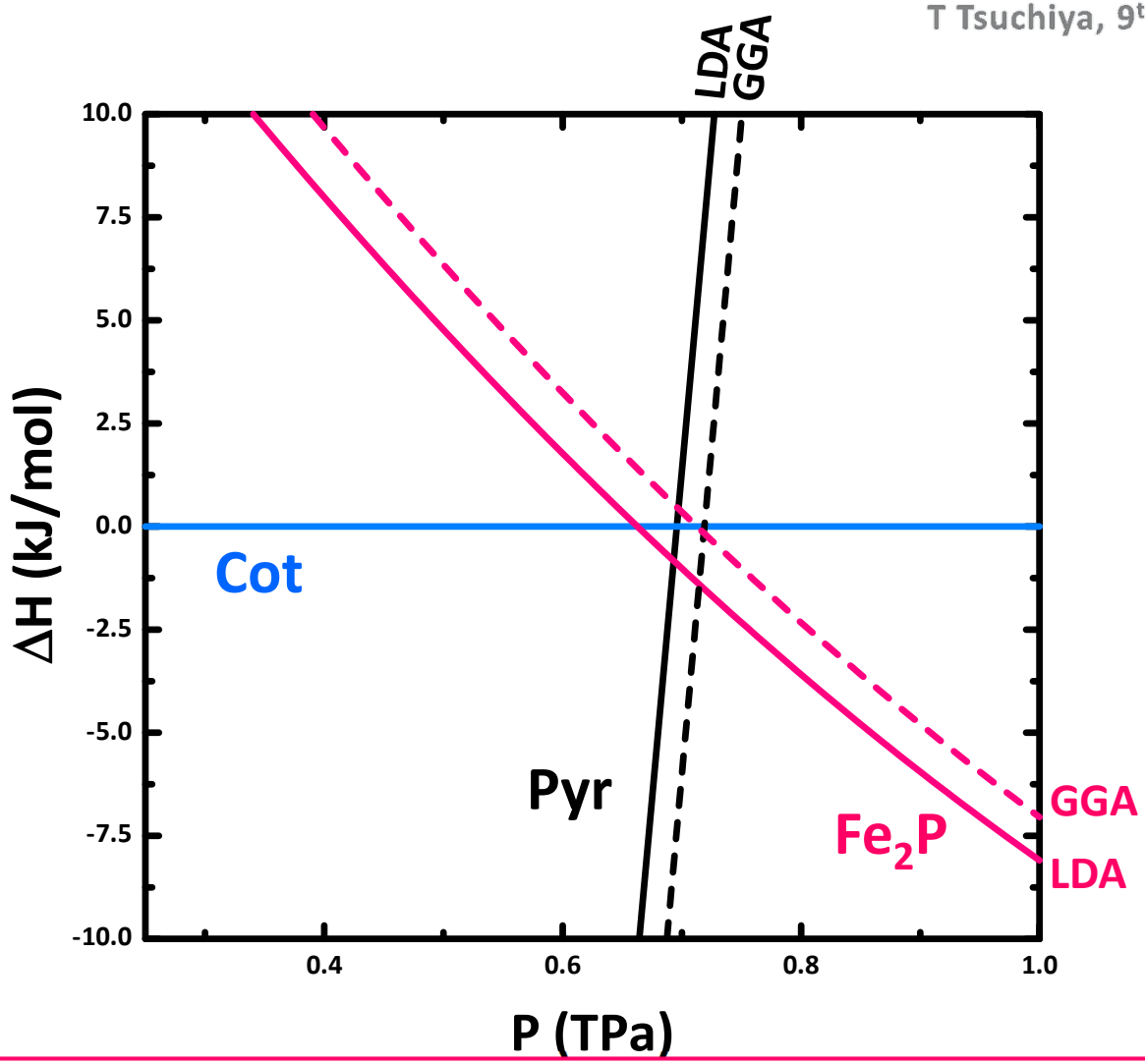
Coordination numbers in parentheses

Static enthalpy differences relative to the pyrite phase



$$H(P) = E_{tot}(P) + PV$$

Tsuchiya & Tsuchiya (2011)



- **Pyrite directly transforms to the Fe_2P-type phase (not cotunnite) at ~7 Mbar!**

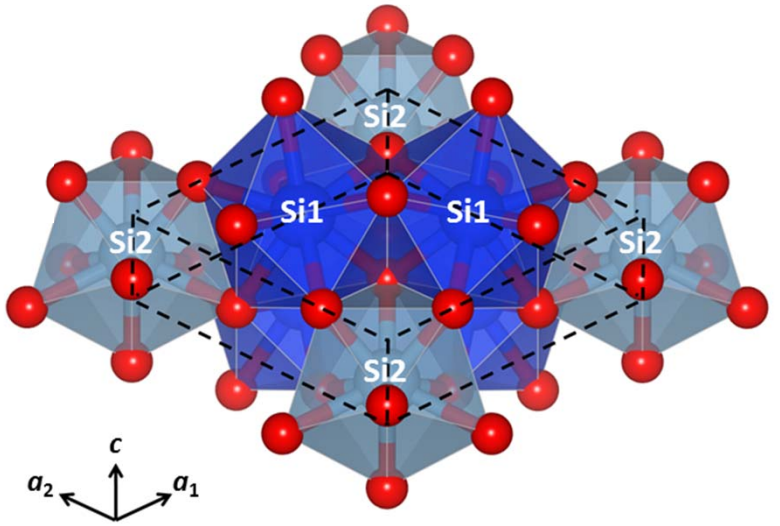
- No other stable structures
- No elemental dissociation of SiO_2 into Si (hcp) plus O_2 (ζ), either

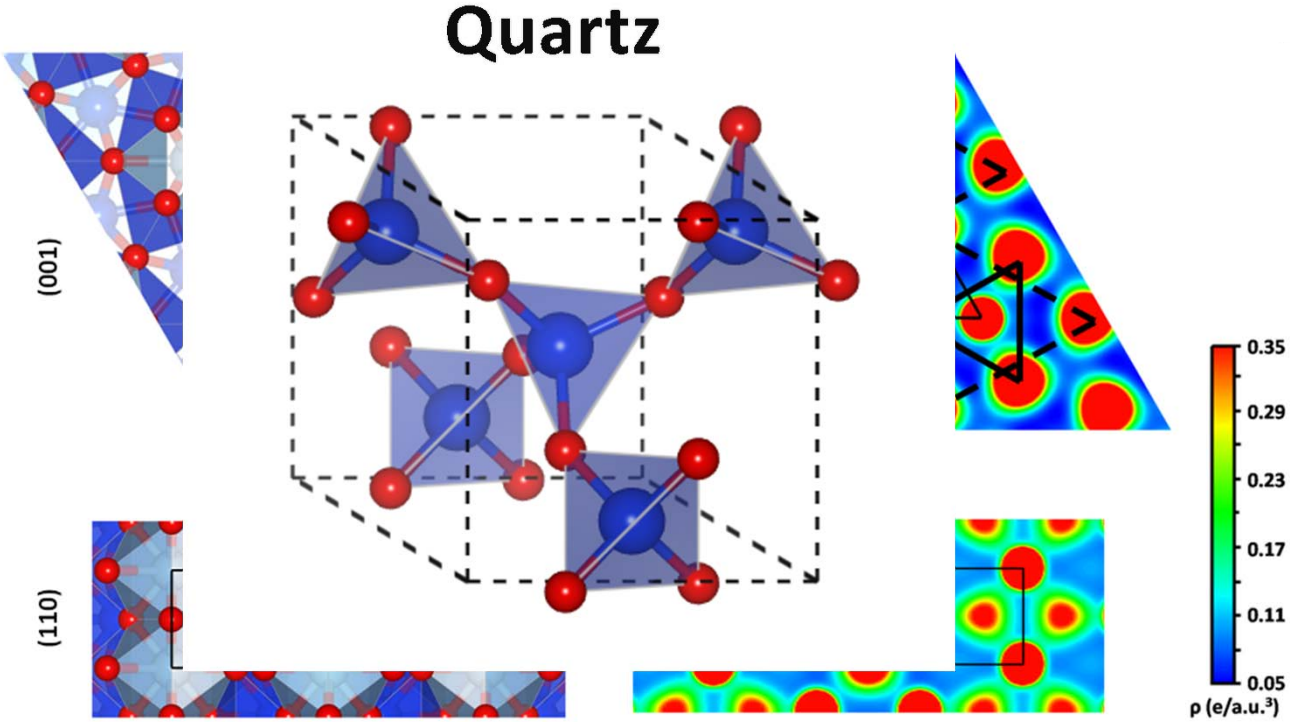
Tsuchiya & Tsuchiya (2011)

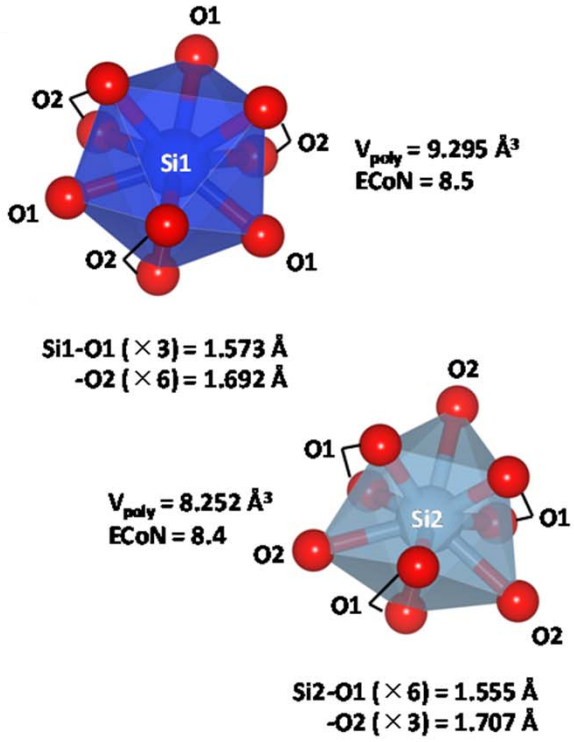
Crystal structure of the Fe_2P-type new high-*P* phase of SiO_2

Tsuchiya & Tsuchiya (2011) PNAS

- Hexagonal cell ($P\bar{6}2m, Z = 3$) with two different kinds of **SiO_9 tricapped trigonal prisms**
- Those polyhedra are fairly regular. This makes the structure more stable than Cot.

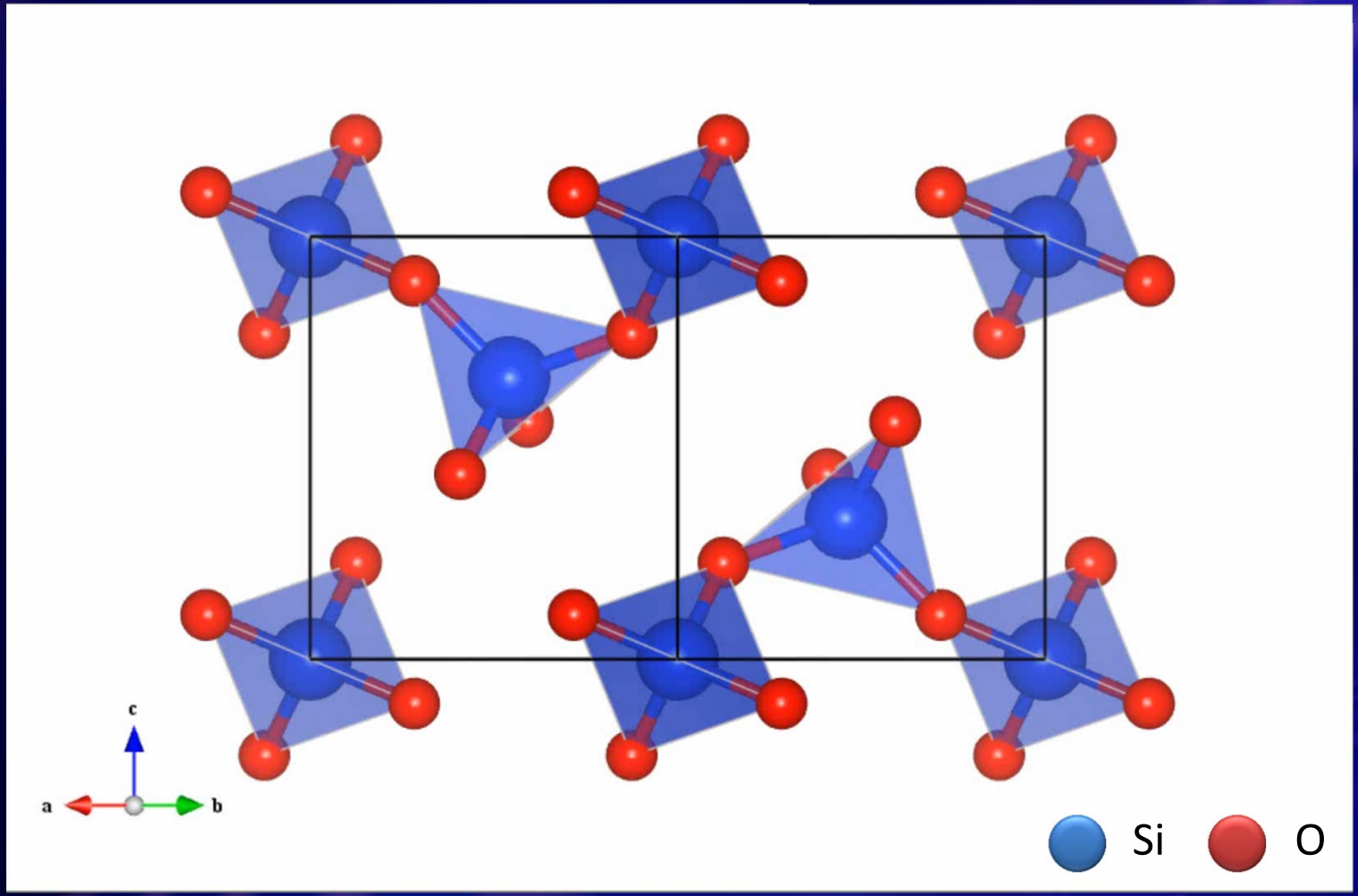




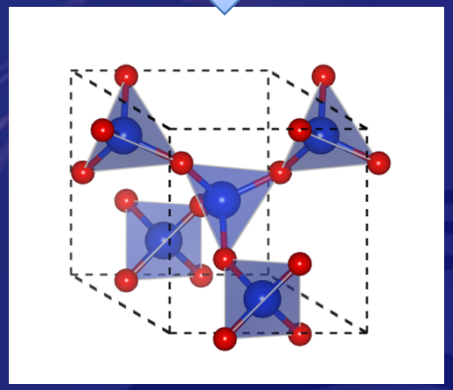


SiO_2 Quartz

Tsuchiya & Tsuchiya (2011) PNAS

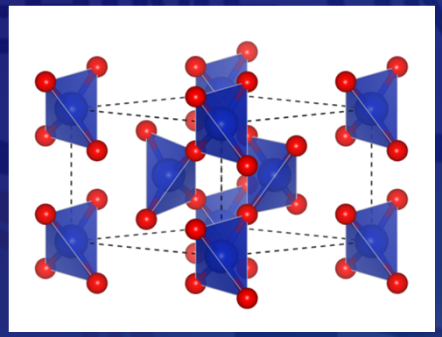


Qz → Fe_2P



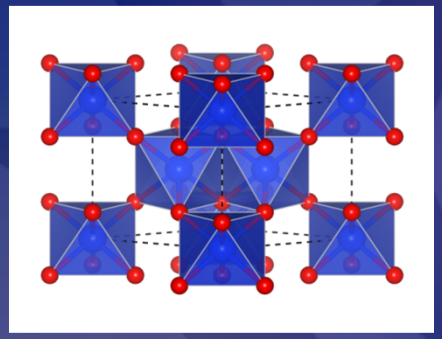
(1) Quartz

SiO_4



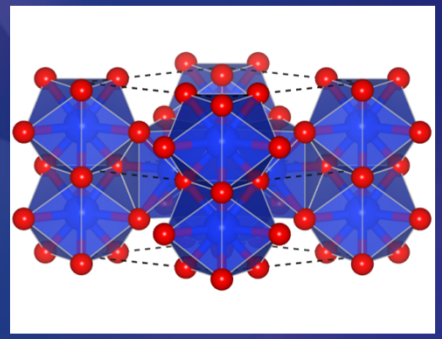
(2) *P*2
(metastable)

SiO_{4+6}



(3) Li_2ZrF_6-type
(metastable)

SiO_6

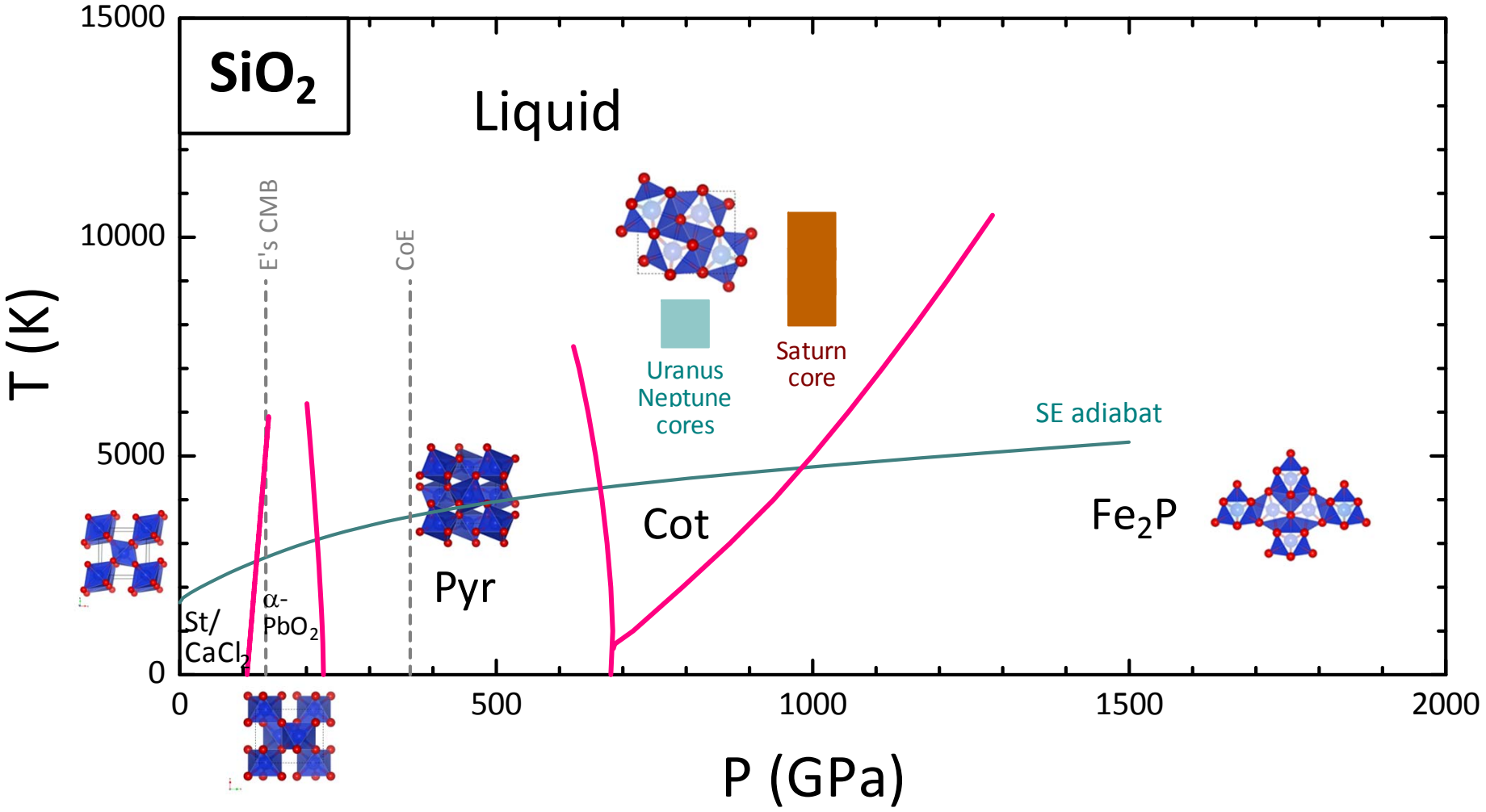


(4) Fe_2P-type
(stable >~700 GPa)

SiO_9

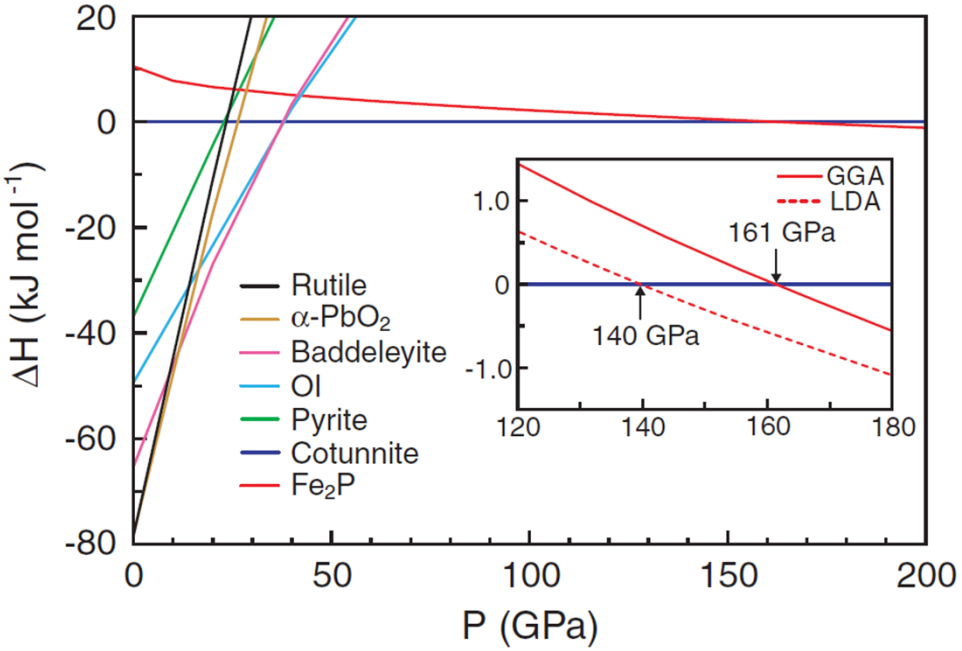
Tsuchiya & Tsuchiya (2011)

Ultrahigh-*P*,*T* phase relations in SiO_2



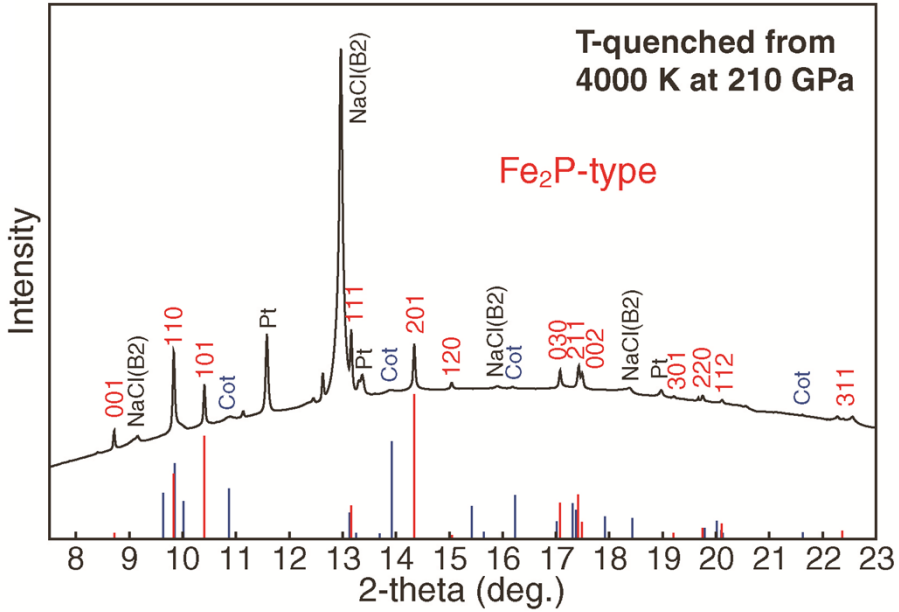
Tsuchiya & Tsuchiya (2011) PNAS

Experimental confirmation using a low-*P* analog, TiO_2



Low-transition pressure from cotunnite-type to Fe_2P-type at ~150 GPa and 0 K

Successful experimental identification by LH-DAC at SPring-8



Dekura, Tsuchiya+ (2011) PRL

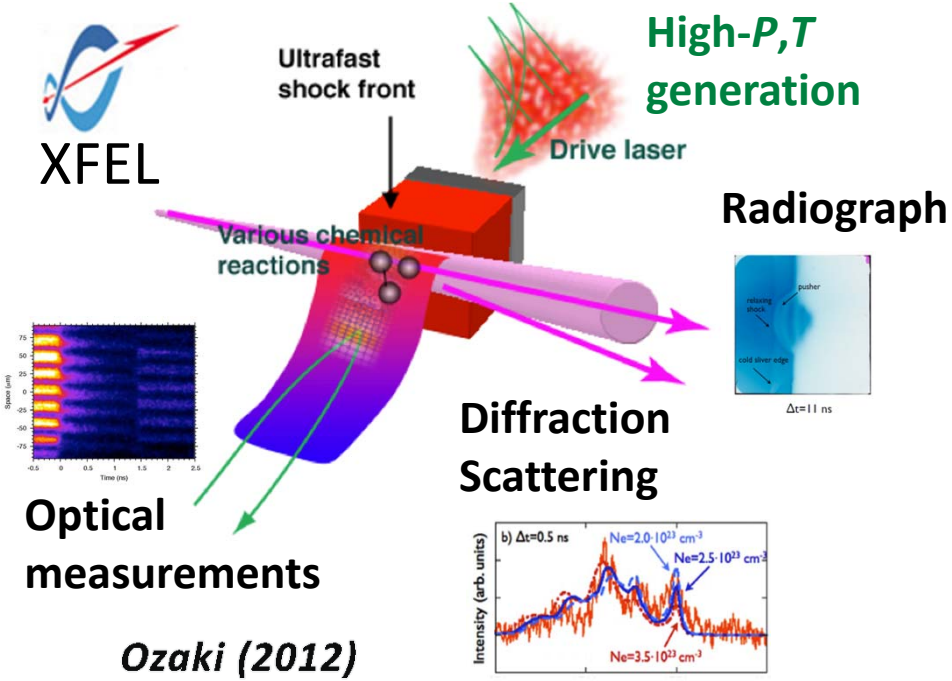
Experimental confirmation

- Laser shock technique
- Magnetic shock (Z-machine)

USA, France, …

A new project in Japan at Spring-8

XFELとパワーレーザーによる
新極限物質材料の探索



K. Tanaka, N. Ozaki, O. Sakata,
T. Tsuchiya, T. Sano, T. Sekine,
K. Arakawa, … (>20 people)

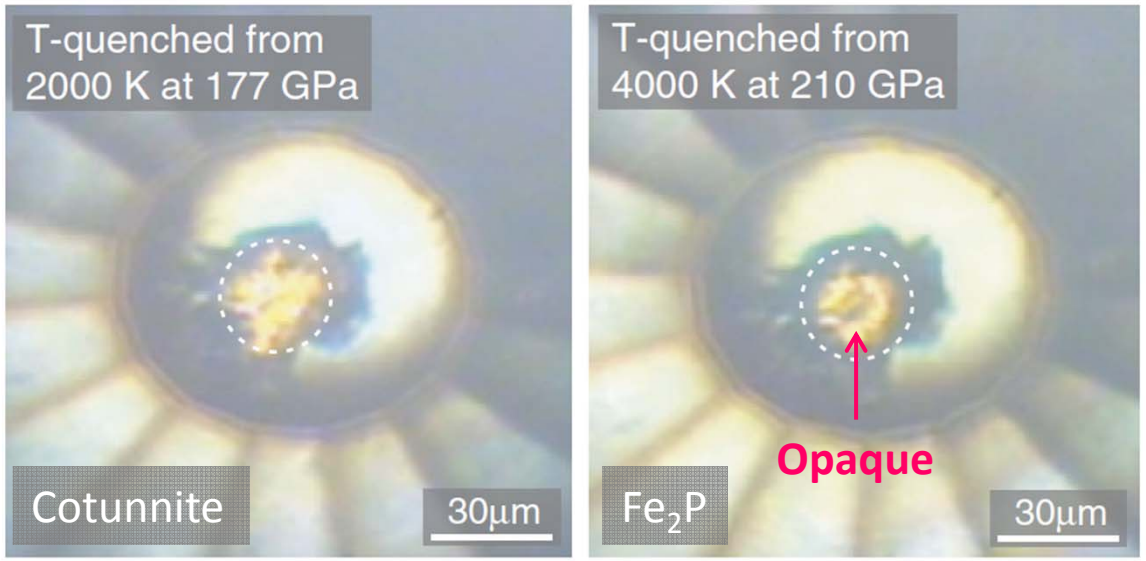
Osaka Univ., NIMS, Ehime Univ., Hiroshima Univ., Shimane Univ., …

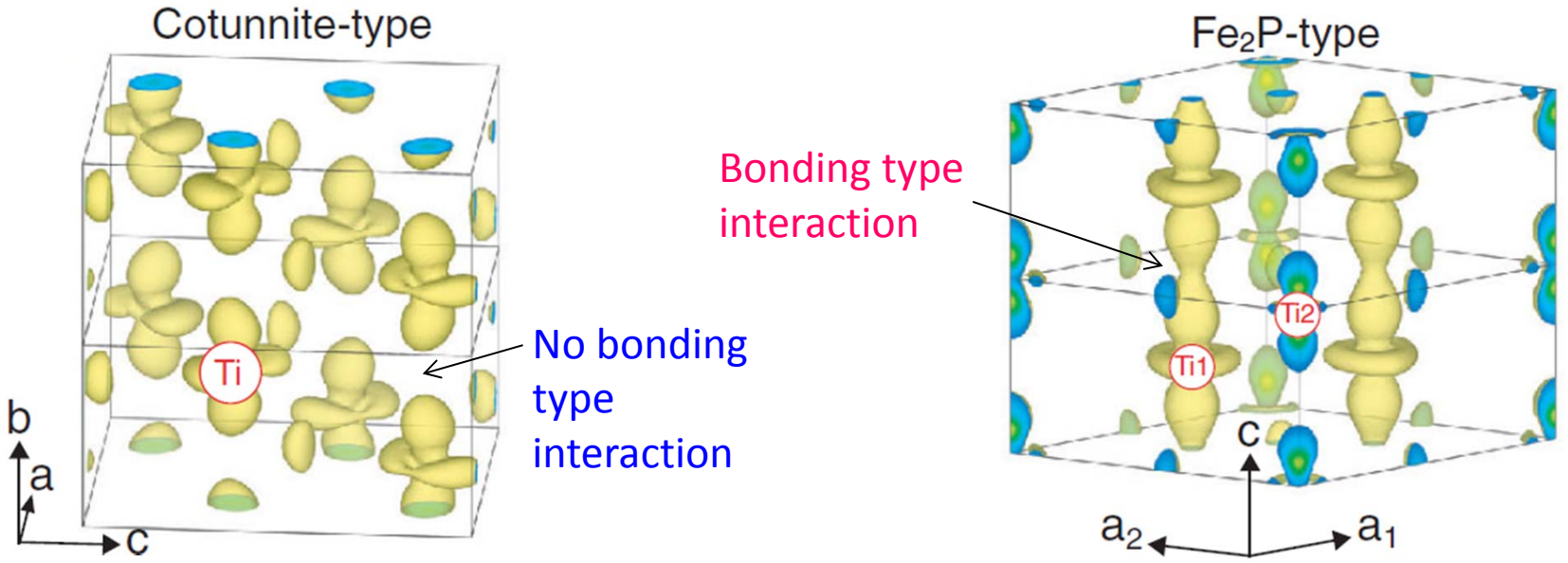
X-ray Free Electron Laser (XFEL)

In situ observation in TPa regime

Significant optical absorption of Fe_2P-typ TiO_2

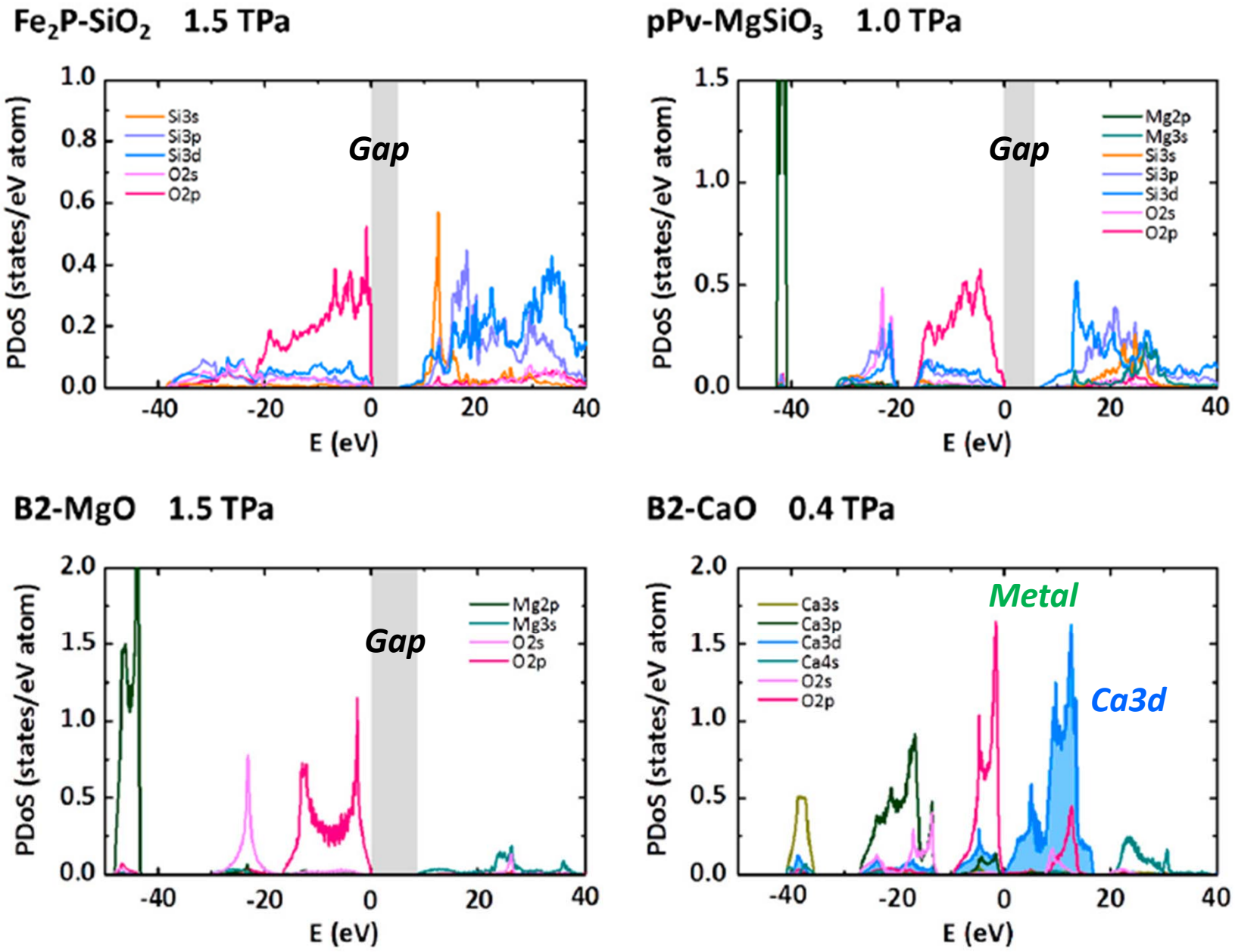
Dekura, Tsuchiya+ (2011) PRL



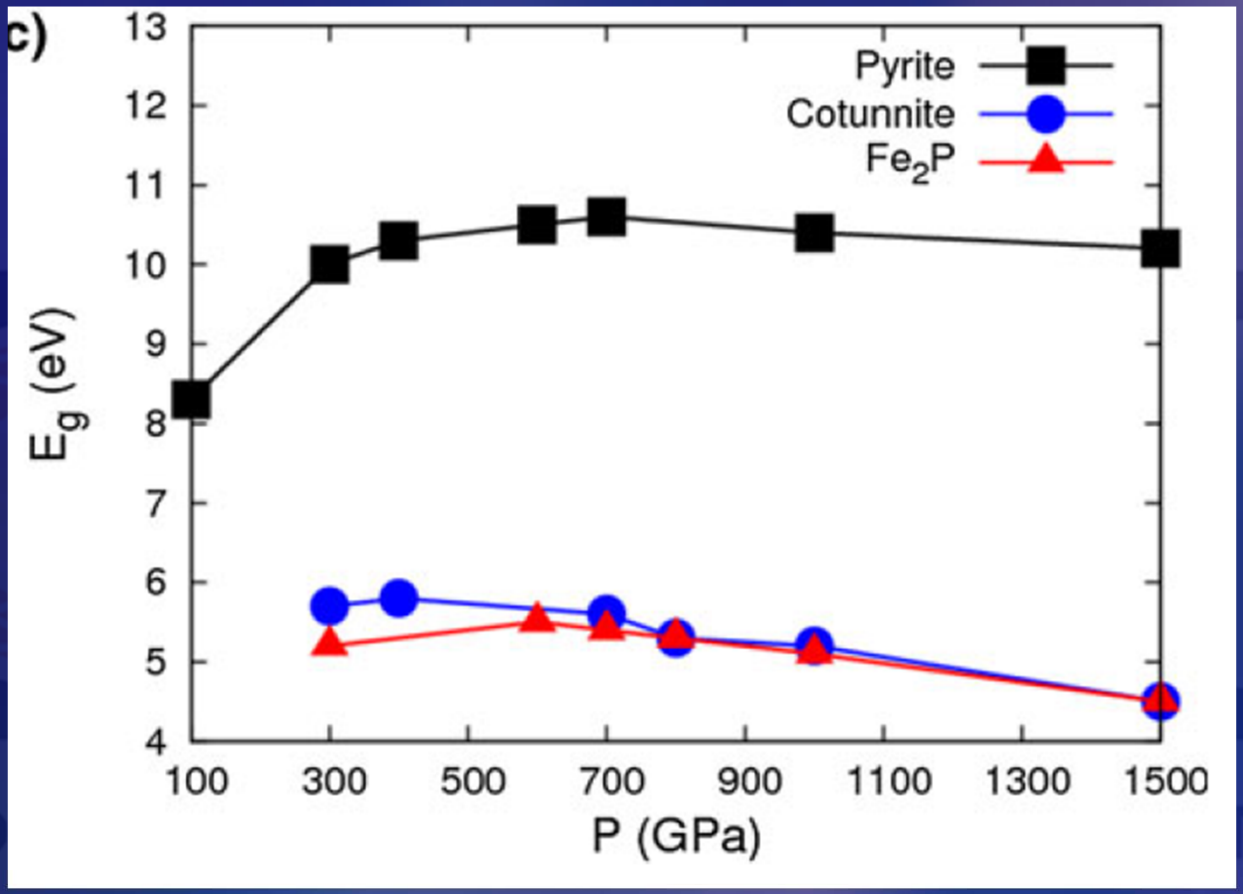


Electronic density of states

Tsuchiya & Tsuchiya (2011) PNAS



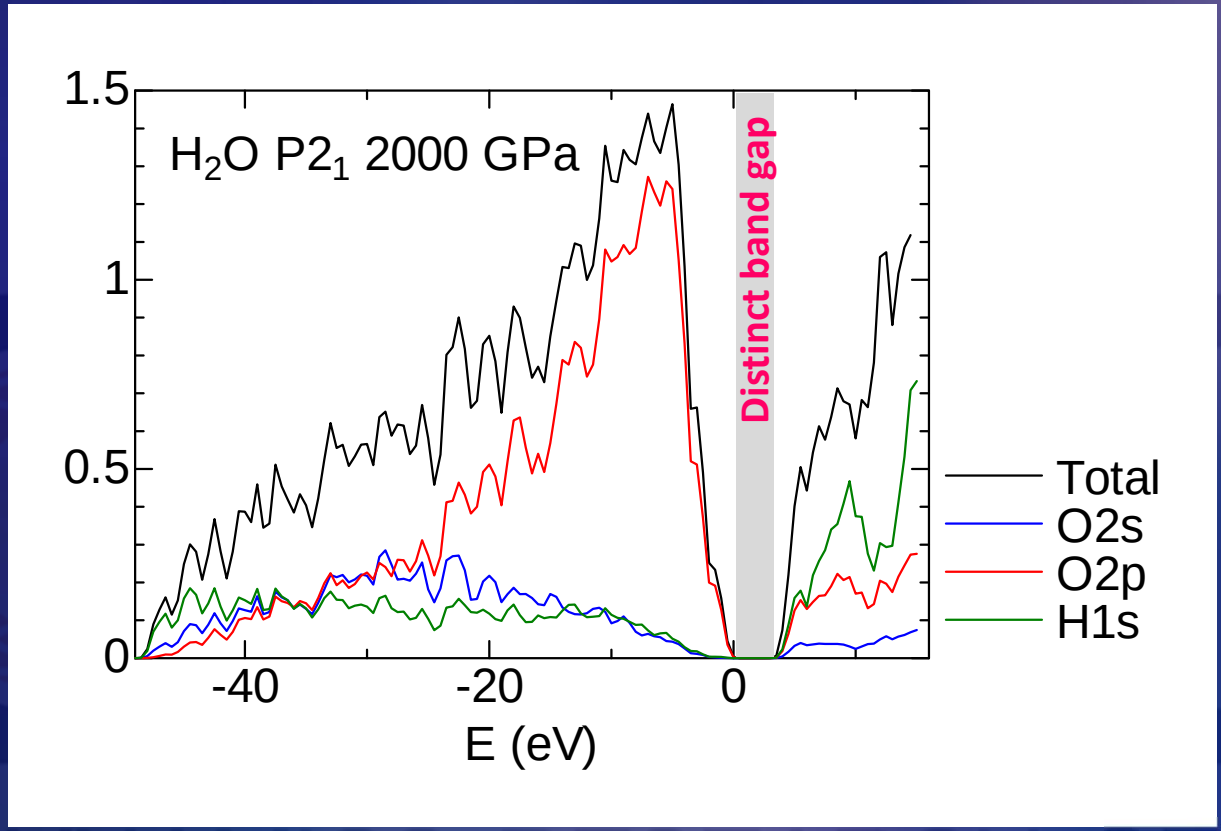
Band gap vs pressure in SiO_2 phases



Metsue & Tsuchiya (2012) Phys Chem Min

Fe_2P-type SiO_2 has much smaller gap than Pyr
but still remains insulating even above 1 TPa.

$P2_1$-type H_2O ice electronic DoS



GEODYNAMICS RESEARCH CENTER

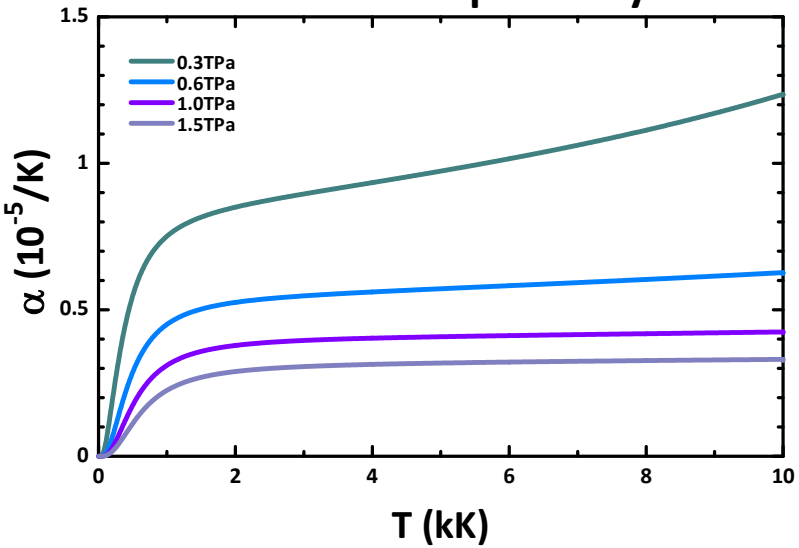
Hermann+ 2012 PNAS
J. Tsuchiya, unpub.

Ice also still remains insulating even at 2 TPa.

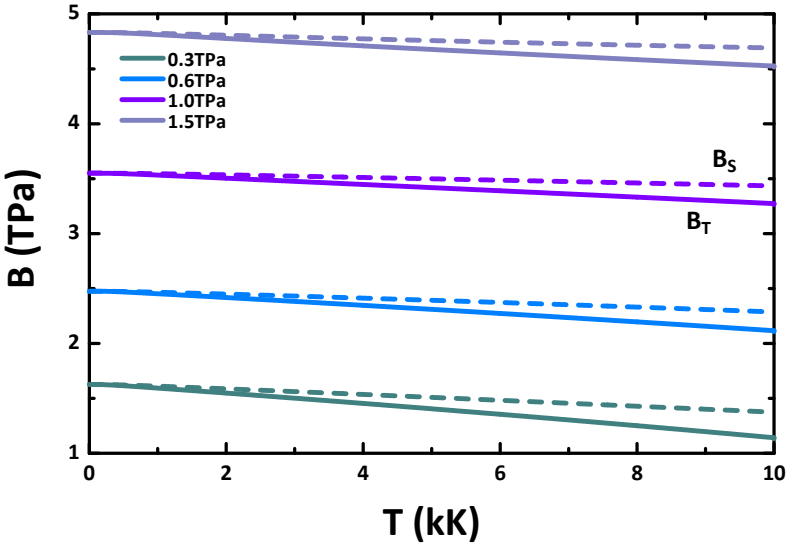
Metallization in solids only for compounds with heavy (*d*) metals

Thermodynamic properties of Fe_2P-type SiO_2

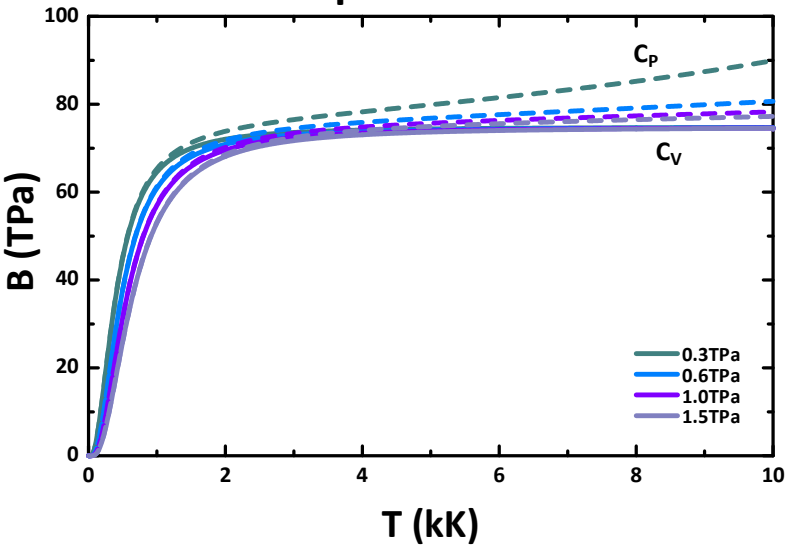
Thermal expansivity



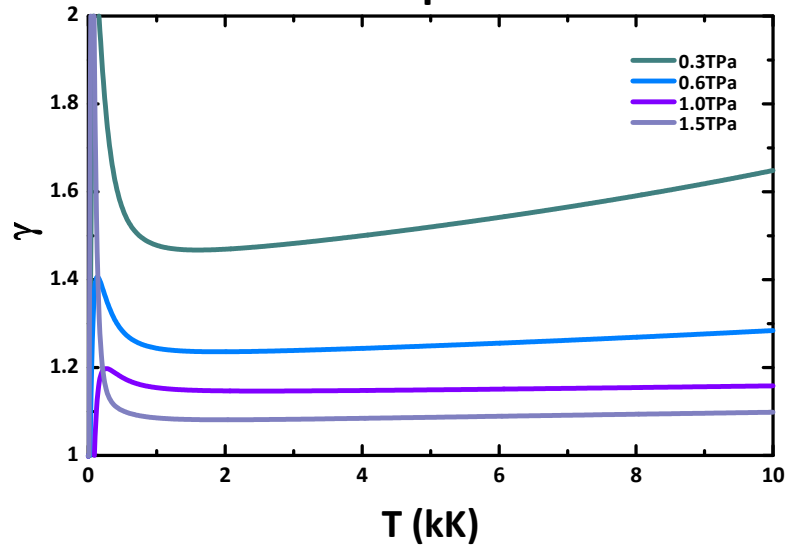
Bulk modulus



Specific heat



Grüneisen parameter



Tsuchiya & Tsuchiya (2011)

Modeling of the silica-rich planetary mantle

Density

$$\frac{\mathrm{d}\rho}{\mathrm{d}r} = \frac{\rho(r)g(r)}{\phi\,(\mathrm{r})}$$

Gravity

$$\frac{\mathrm{d}g}{\mathrm{d}r} = 4\pi G\rho(r) - \frac{2Gm(r)}{r^3}$$

Mass

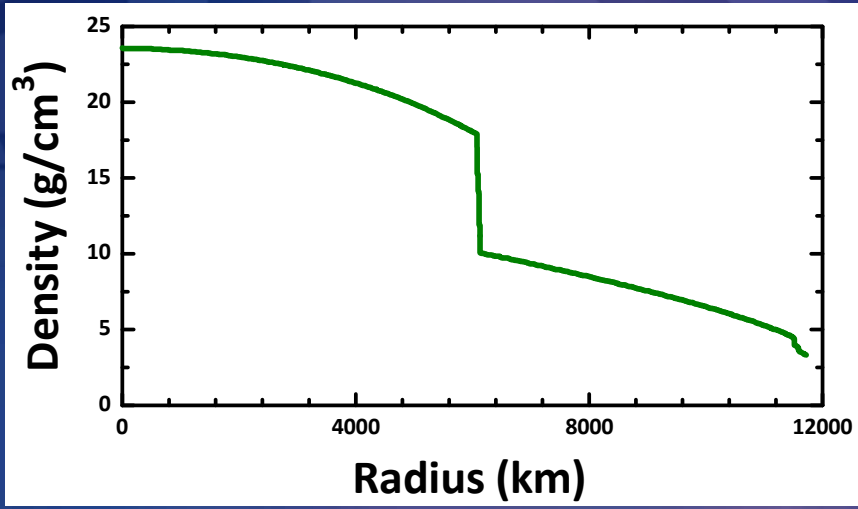
$$\frac{\mathrm{d}m}{\mathrm{d}r} = 4\pi r^2\rho(r)$$

Pressure

$$\frac{\mathrm{d}P}{\mathrm{d}r} = -\rho(r)g(r)$$

$$\phi\,(\mathrm{r}) = B_S(r)/\rho(r)$$

The $\rho - r$ relationship for a super-Earth with $10M_{\oplus}$ evaluated by ***Valencia+ (2006)***

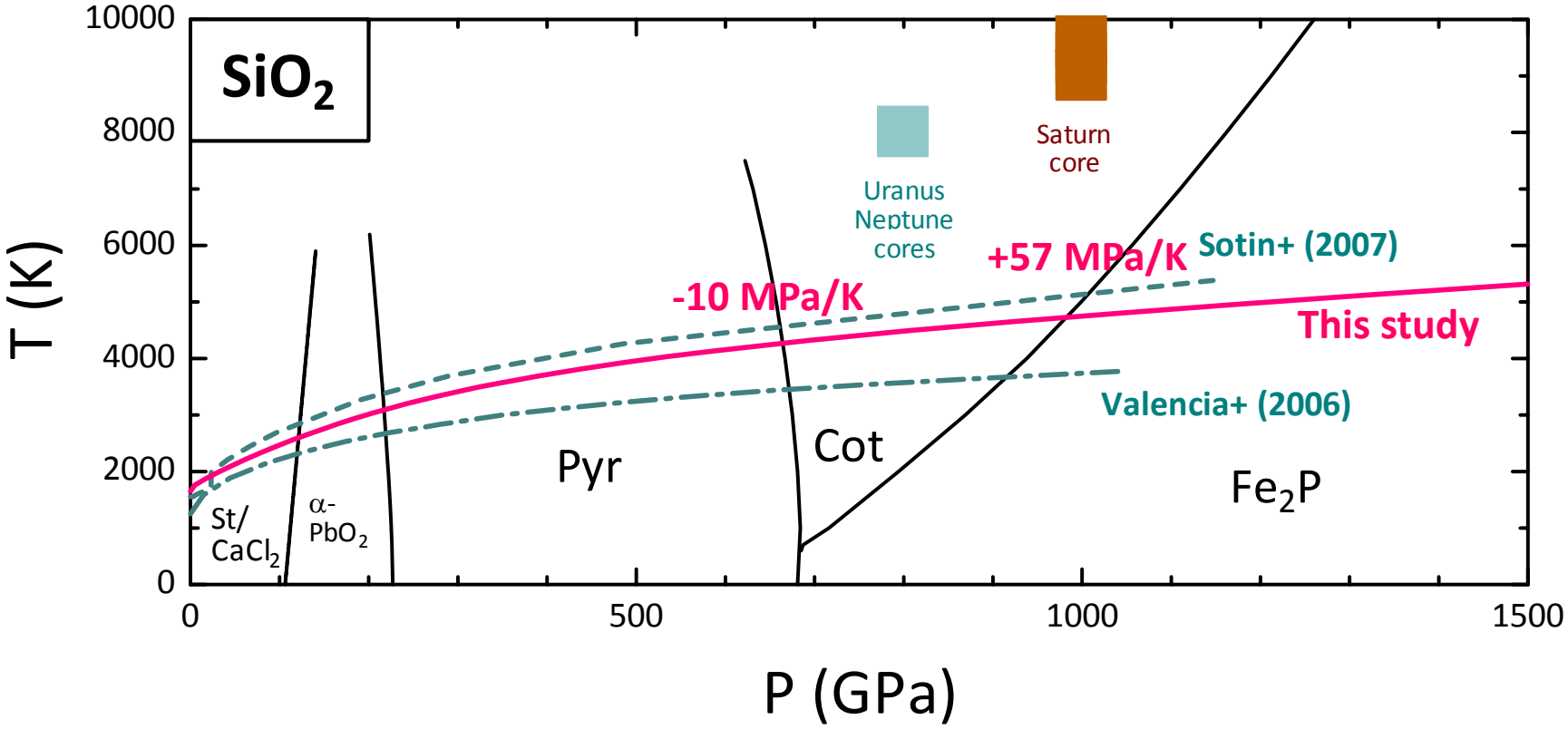


Thermal structure of SE

Adiabatic temperature gradient

$$\left(\frac{dT}{dP}\right)_S = \frac{\alpha(P)g(P)T}{C_P(P)}$$

Almost no difference by using $MgSiO_3$ parameters

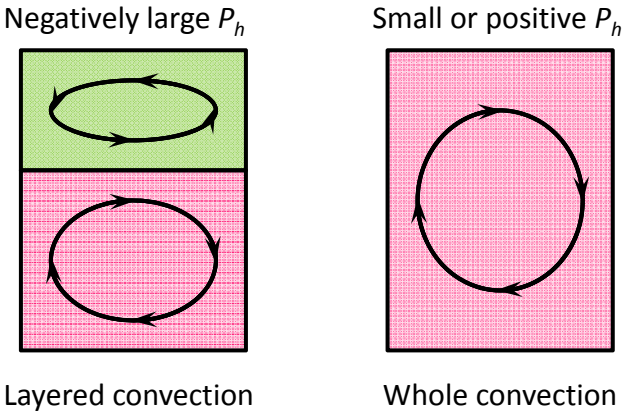


Phase transition buoyancy parameter

Christensen and Yuen (1985)

$$P_h = \frac{\Gamma(\Delta\rho/\rho)}{\alpha\rho g h}$$

For 660-km discontinuity, $P_h \sim -0.2$



For the Pyr-Cot transition in a super-Earth with $10M_\oplus$:

$$\Gamma = -10\ \mathrm{MPa\ K^{-1}}$$
$$\frac{\Delta\rho}{\rho} = 0.04$$
$$\rho = 8400\ \mathrm{kg\ m^{-3}}$$
$$\alpha = 0.53 \times 10^{-5}\ \mathrm{K^{-1}}$$
$$g = 31\ \mathrm{m\ s^{-2}}$$
$$h = 4500\ \mathrm{km}$$

$\Rightarrow$ $P_h \sim -0.064$

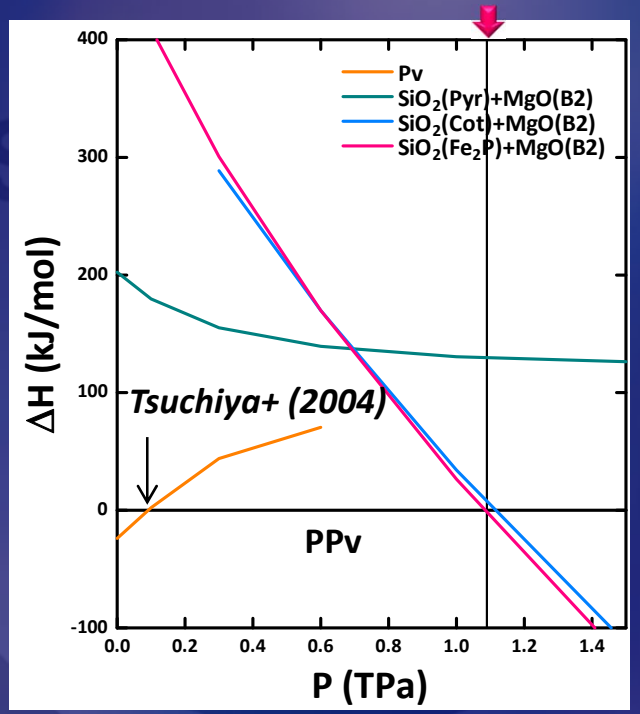
The transition might have not so large effect even with a negative boundary.

Decomposition of $MgSiO_3$ post-perovskite

- $MgSiO_3$ (PPv) → MgO (B2) + SiO_2 (Cot or Fe_2P)
  (Umemoto+ 2006; Tsuchiya & Tsuchiya 2011)
- An intermediate state with $MgSi_2O_5$ + MgO
  (Umemoto+ 2011)
- Disproportionation reaction in $NaCoF_3$

  $NaCoFe_3$ (PPv) → $Na_5Co_3F_{11}$ + $NaCo_3F_7$
  (Yusa+ 2012)

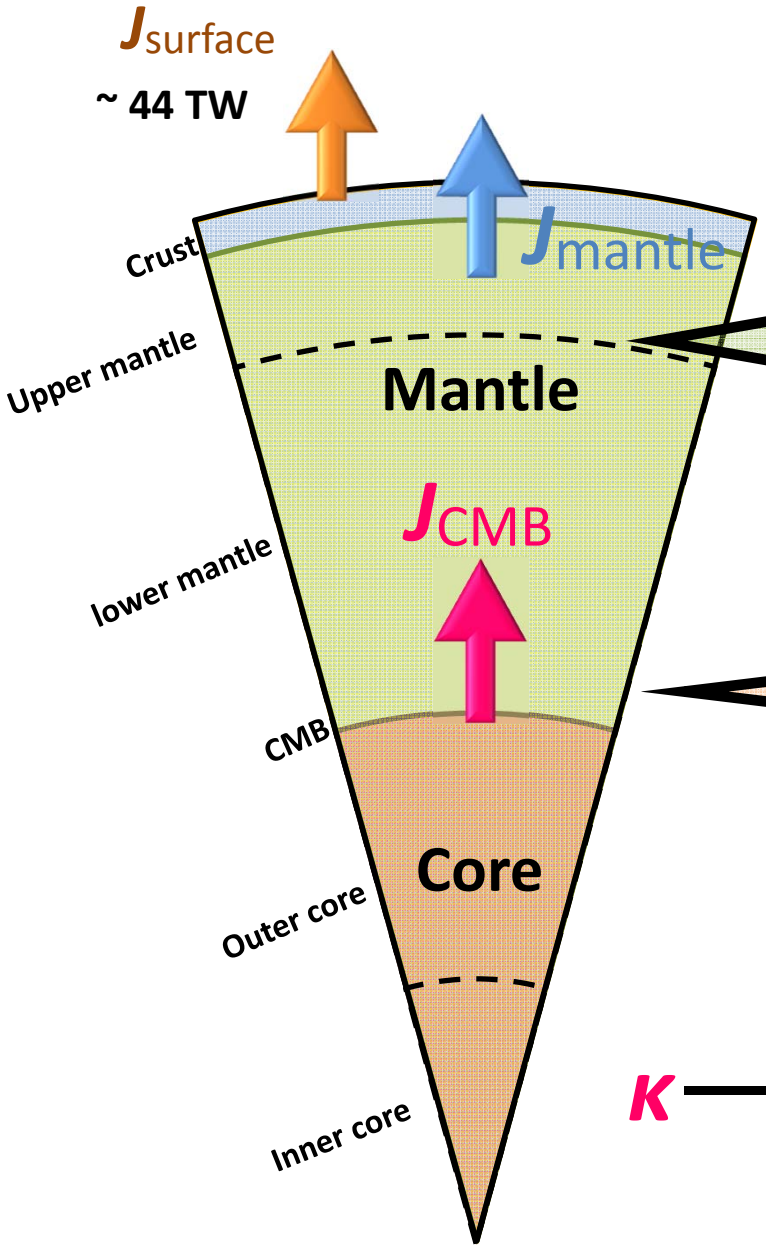
Tsuchiya & Tsuchiya (2011)



Further studies with careful structure search maybe needed

But no eccentric changes such as metallization seem likely.

Energy transportation in the Earth



Mantle convection

Rayleigh number

$$Ra = (\alpha g \Delta T C_p \rho^2 z^3)/(v\kappa)$$

→ Convection style

CMB heat flux

$$q = -\kappa \Delta T/\delta_{TBL}$$

$$J_{CMB} = \int q \, da$$

→ Geodynamo

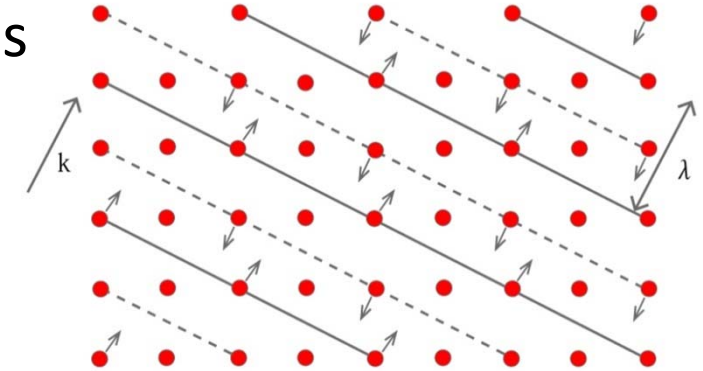
→ Inner core growth

κ

- **Lattice conductivity**
  Propagation of photon
- **Radiative conductivity**
  Emission of photon

Lattice thermal conductivity

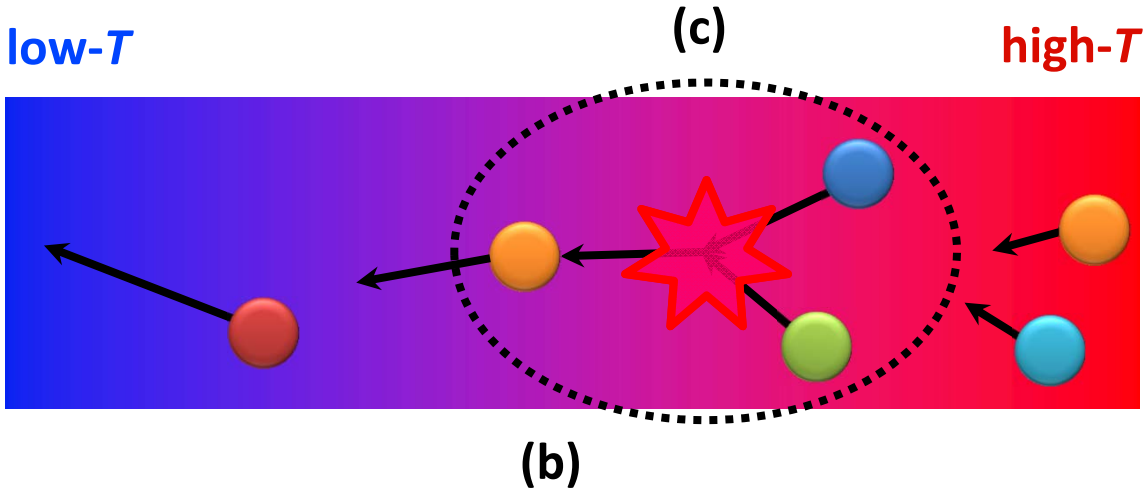
(a) Phonon = Quantized lattice vibrations



(b) Phonon-phonon scattering → Thermal resistivity

(c) Anharmonicity → Interaction of phonons

Density functional perturbation theory (DFPT)



Lattice thermal conductivity (Higher order anharmonic lattice dynamics)

$$\kappa = \frac{1}{3}\sum_{s}^{3n}\int \mathbf{v}_{\mathbf{q},s}^{2} c_{\mathbf{q},s}\tau_{\mathbf{q},s} d\mathbf{q}$$

Harmonic quantities

$\mathbf{v}_{\mathbf{q},s}$	$c_{\mathbf{q},s}$
Phonon group velocity	Mode specific heat

Anharmonic phonon

Phonon lifetime

$$\tau_{\mathbf{q},s} = \frac{1}{2\Gamma(\omega_{\mathbf{q},s})}$$

Bose-Einstein function

$$n_{\mathbf{q}j} = \frac{1}{e^{\hbar\omega_{\mathbf{q}j}/k_B T} - 1}$$

Phonon damping function

$$\Gamma_{\mathbf{q}j}(\omega) = \frac{\pi}{2}\sum_{\mathbf{q}',j',j''} |V_3(-\mathbf{q}j,\mathbf{q}'j',\mathbf{q}-\mathbf{q}'j'')|^2 \{[1+n_{\mathbf{q}'j'} + n_{\mathbf{q}-\mathbf{q}'j''}]\delta(\omega_{\mathbf{q}'j'}+\omega_{\mathbf{q}-\mathbf{q}'j''}-\omega) + 2[n_{\mathbf{q}-\mathbf{q}'j''} - n_{\mathbf{q}'j'}]\delta(\omega_{\mathbf{q}'j'}-\omega_{\mathbf{q}-\mathbf{q}'j''}-\omega)\}.$$

***V_3*: anharmonic coupling coefficient**

Previous works on κ

Ab initio (non-equilibrium) molecular dynamics (MD), etc

→ **Large simulation cell size**

→ **High computational cost**

Limited to simple crystal structures like MgO

(de Koker 2009; Tang & Dong 2010; etc)

Our technique

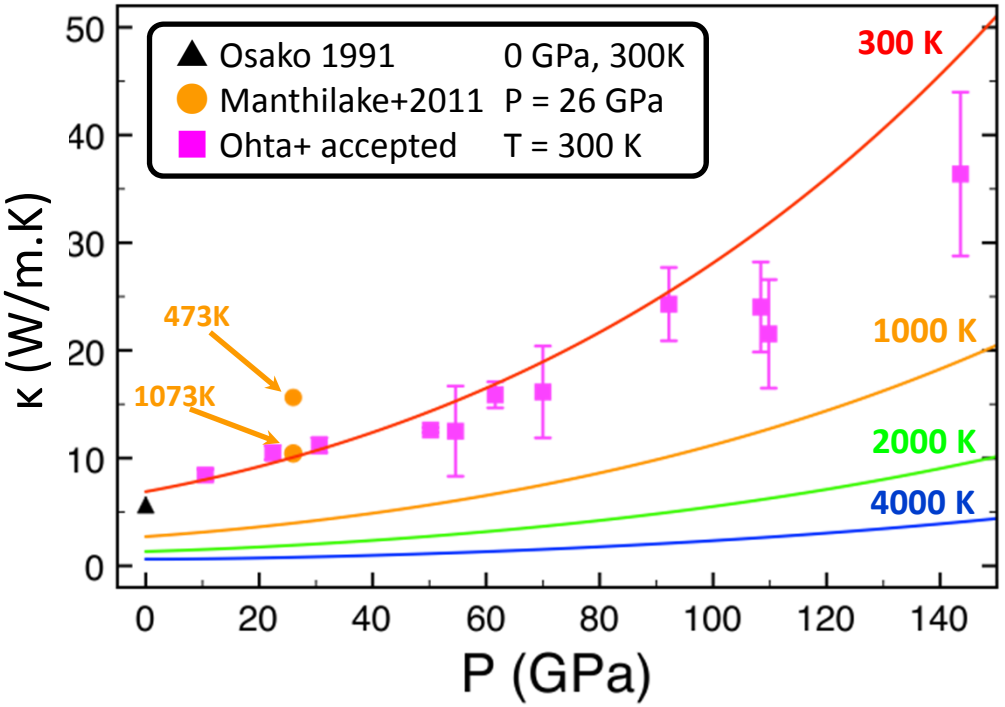
DFPT approach

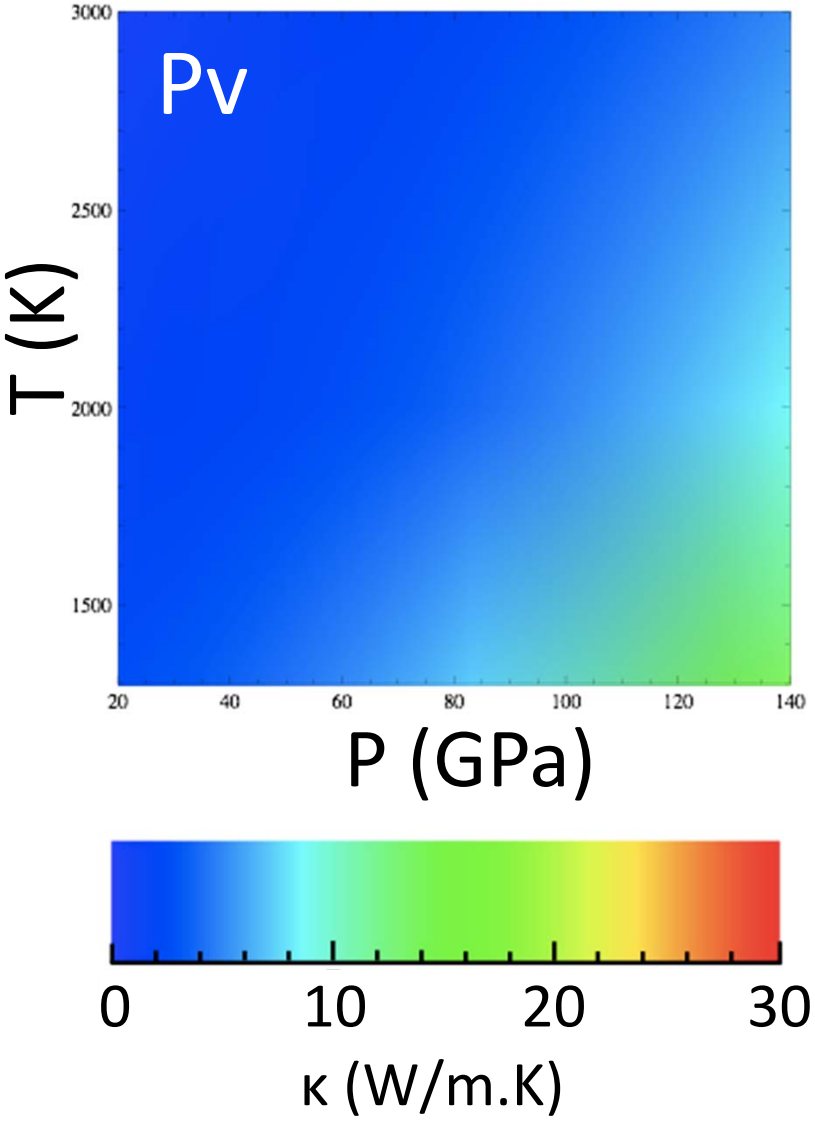
→ **Small (primitive) unit cell size**

→ **High efficiency & low numerical error**

Applicable to complex structures like $MgSiO_3$

κ of $MgSiO_3$-Pv





Lattice thermal conductivity rapidly increase with increasing pressure.

$$\kappa_{\mathrm{Pv}}(2900\ \mathrm{km}) \sim 3\kappa_{\mathrm{Pv}}(660\ \mathrm{km})$$

Dekura, Tsuchiya, Tsuchiya, PRL, under review

Rayleigh number of mantles

$$Ra = \alpha g \Delta T \rho^2 C_P z^3 / (\nu \kappa)$$

Earth

$\Delta T = 500$ [K]

$\nu \sim 10^{21} - 10^{23}$ [Pa s]

Mitrovica & Forte (2004)

$\kappa \sim 2 - 7$ [W m^{-1}K^{-1}]

This study

Super-Earth with 10$M_\oplus$

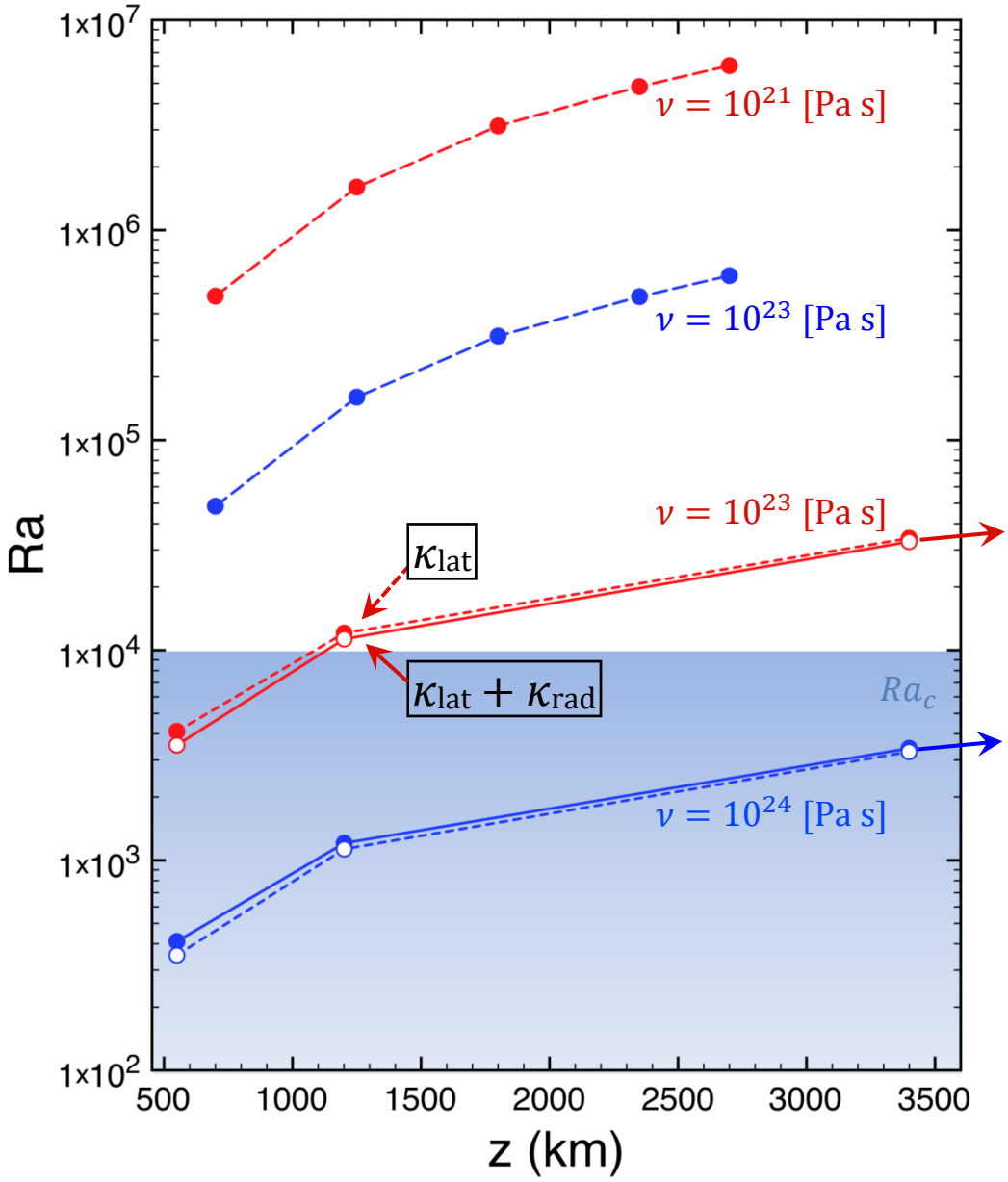
$\Delta T = 500$ [K]

$\nu \sim 10^{23} - 10^{24}$ [Pa s]

$\kappa \sim 4 - 200$ [W m^{-1}K^{-1}]

This study

⇒Mantle convection maybe significantly suppressed
(Consistent with a recent modeling by *Stamenkovic+ 2011*)

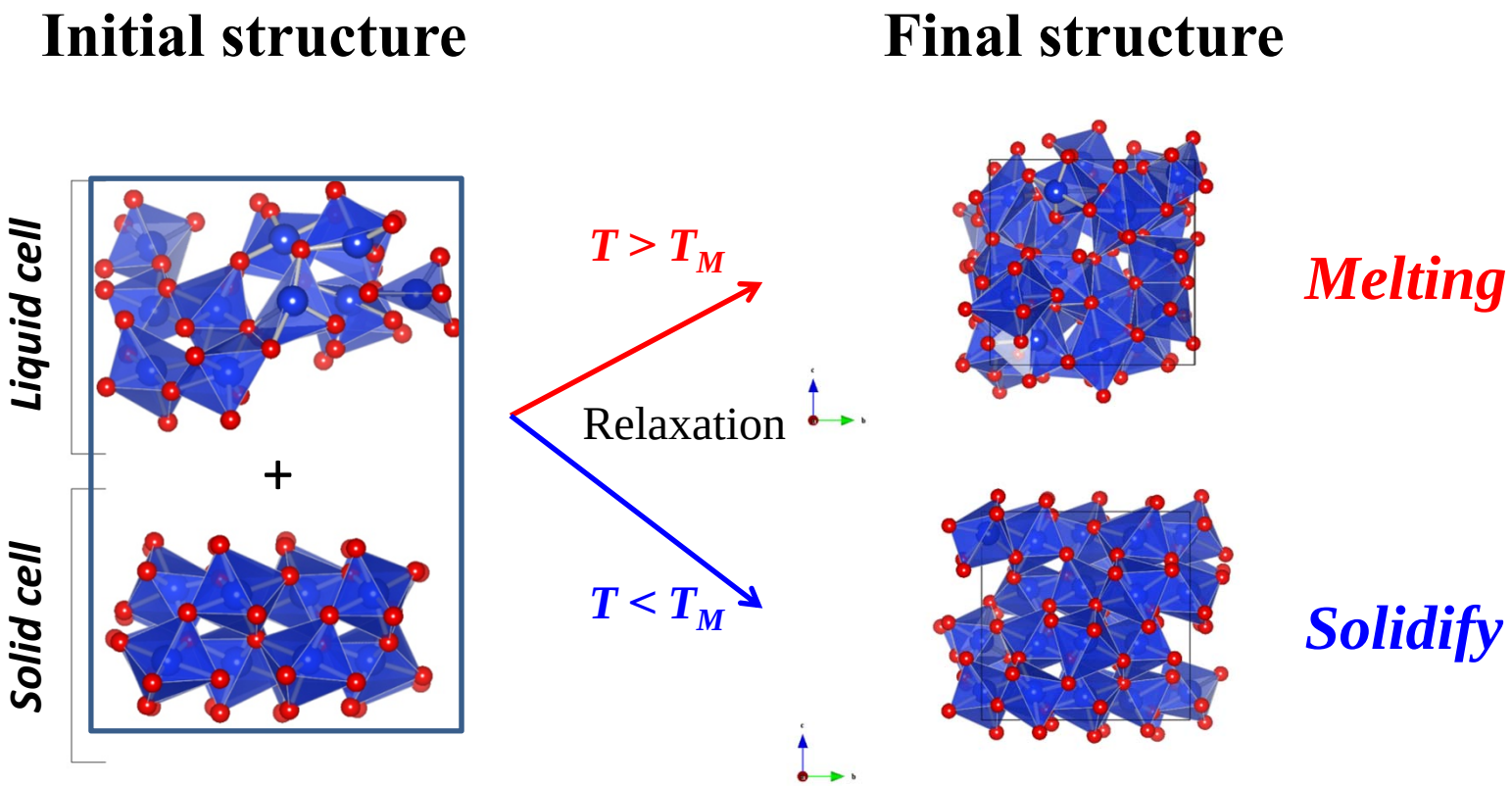


Dekura+ in prep.

Melting temperature

Ab initio two-phase coexisting MD *(Alfe 2009; Usui & Tsuchiya 2010; etc)*

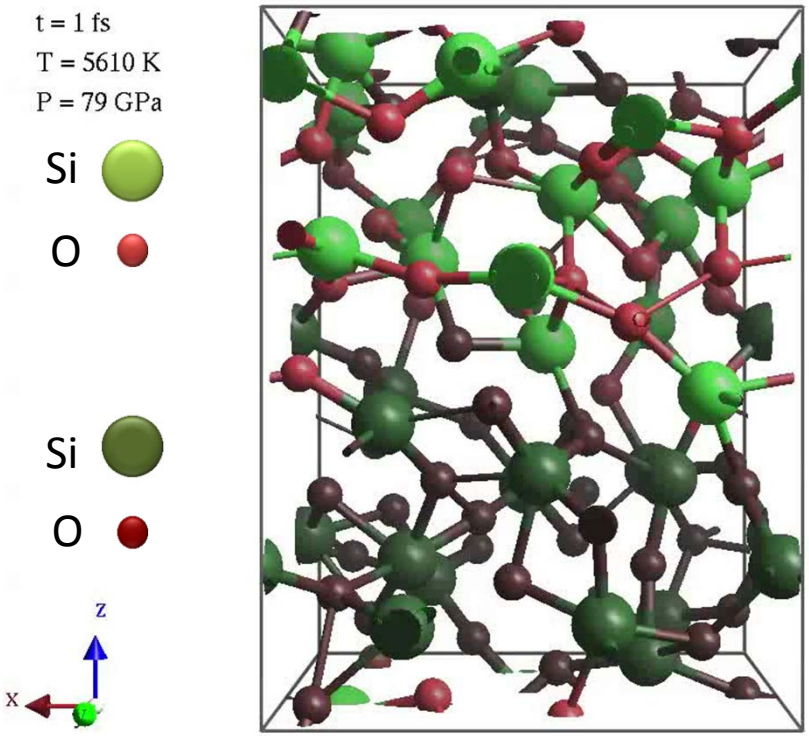
- *Equilibrate a supercell with **Sol-Liq interfaces** at several P,T conditions*
- *A method to avoid the kinetic effects (super-cooling and -heating) across melting and freezing*



Ex) SiO_2 stishovite

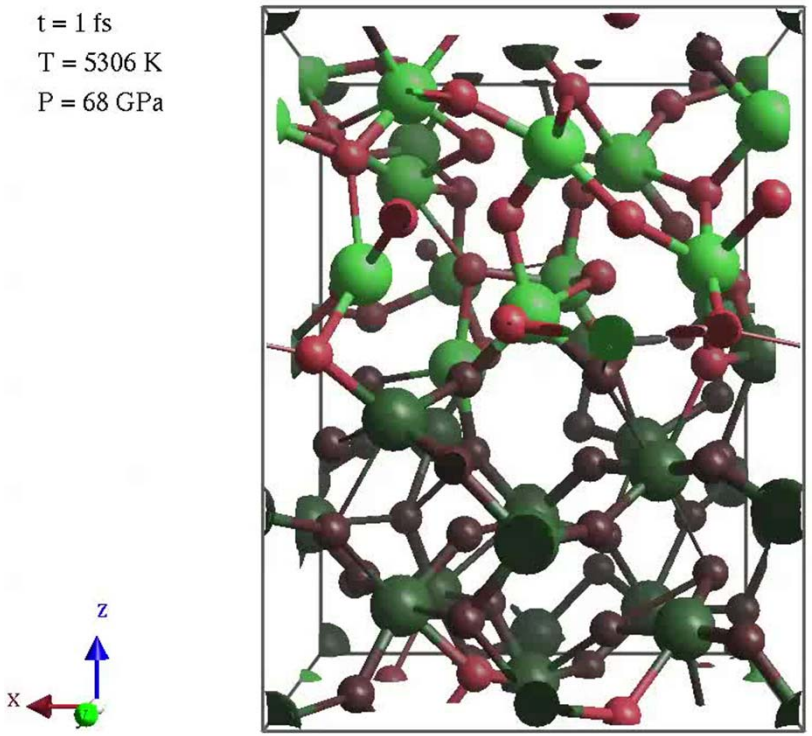
Usui & Tsuchiya (2010) J Earth Sci

a) $T > T_M$ Melt stable



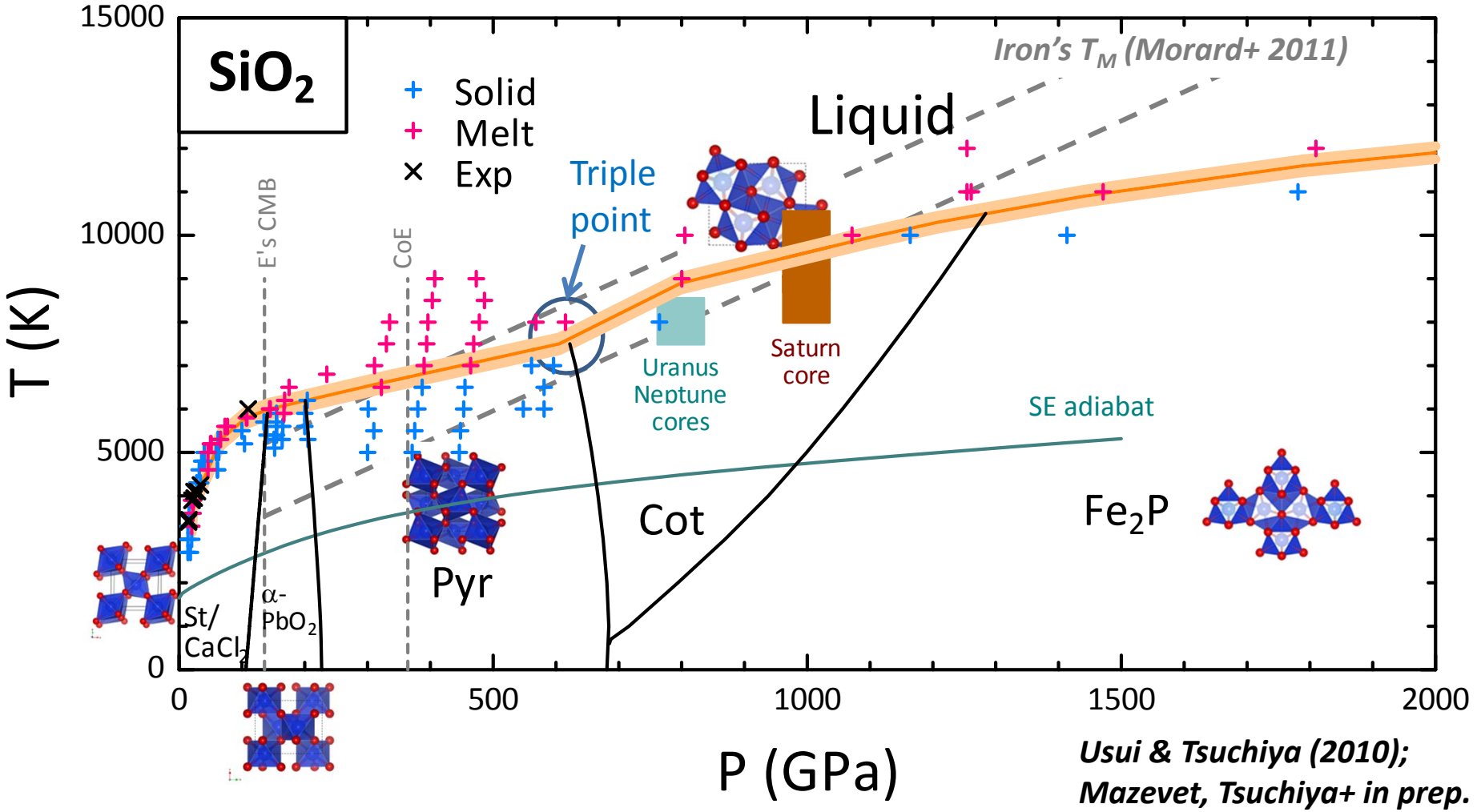
P = 73 GPa, T = 5,600 K

b) $T < T_M$ Solid stable



P = 62 GPa, T = 5,300 K

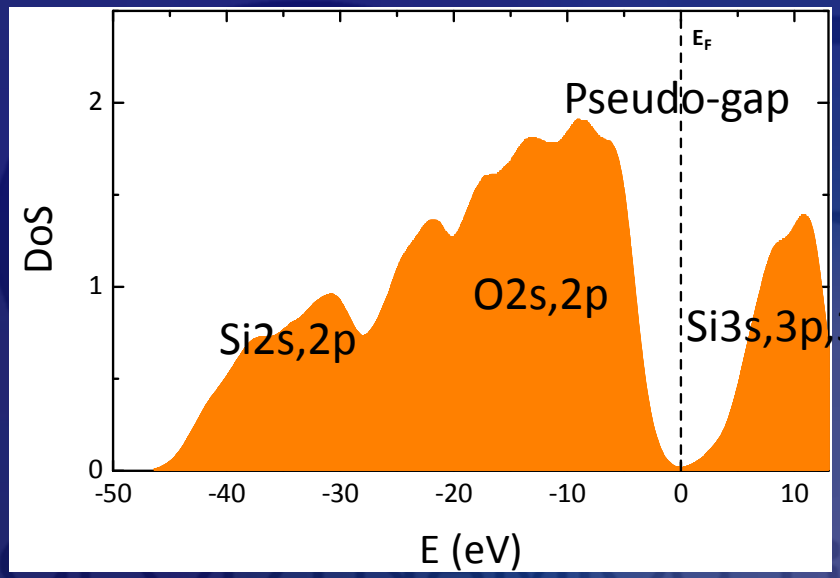
Melting curve of SiO_2



T_M quite comparable to the core conditions of some planets

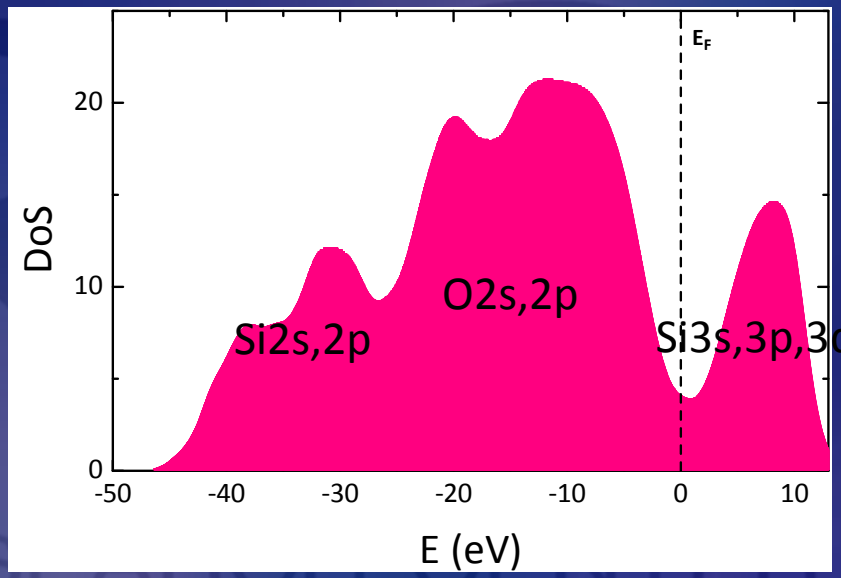
Electronic DoS of silicate melt

Subsolidus condition
(1800 GPa, 10000 K)
Fe_2P-type SiO_2



Semi-metallic

Supersolidus condition
(1800 GPa, 12000 K)
Liquid SiO_2

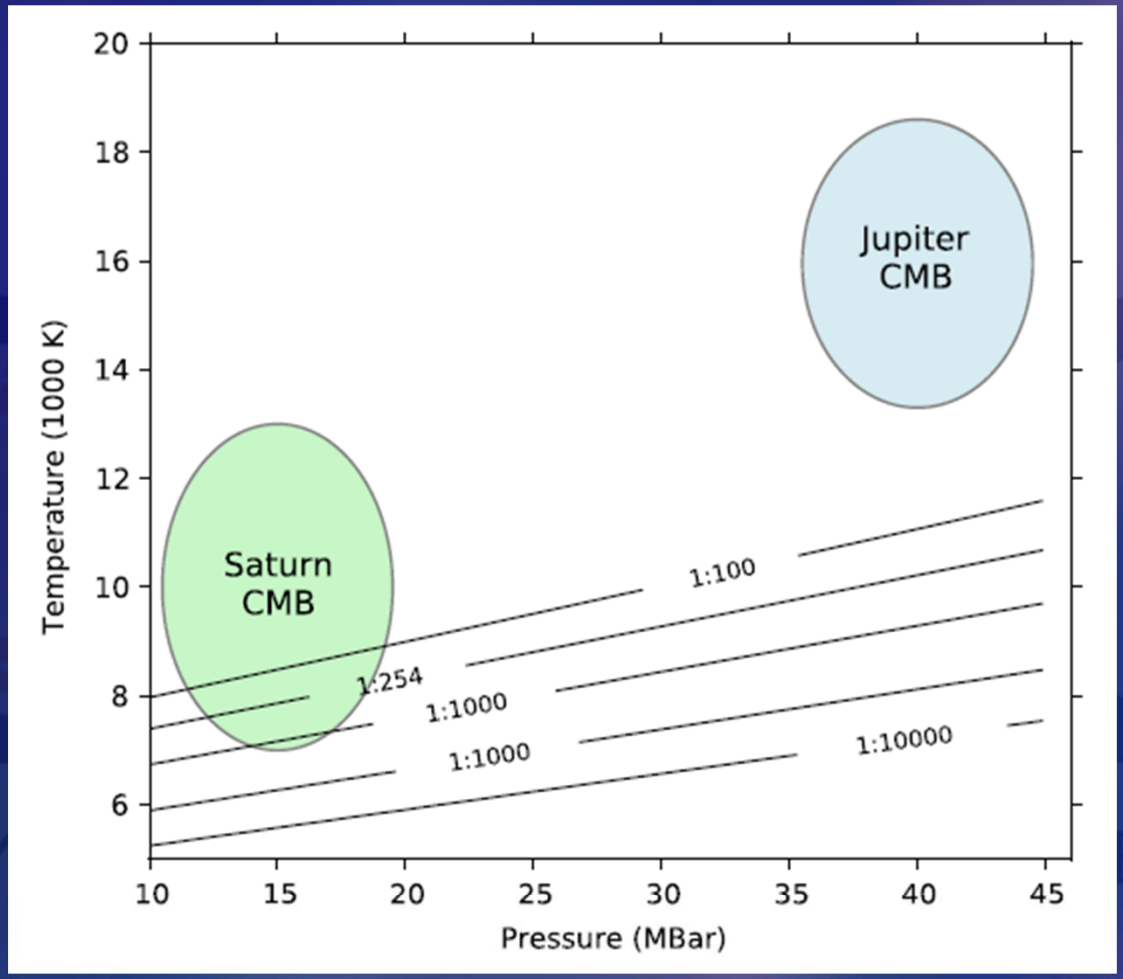


Metallic

Metallization (band gap closure) across melting ***(cf. Karki 2007 PRB)***

Liquid silicate maybe easily mix with H or H_2O. → ***Core erosion (cf. Wilson+ 2012 PRL)***

Solubility of oxide into liquid H

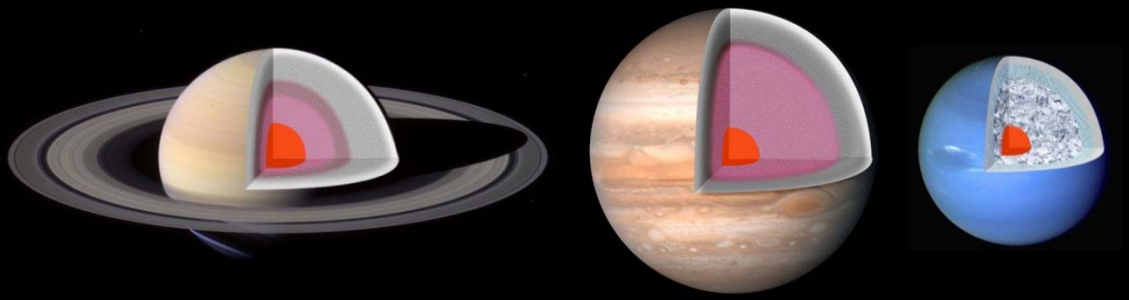


Wilson & Militzer (2012) PRL

Oxides soluble to liquid H at $T_{\text{gass giant}}$ but not at T_{SE}

Current views

Gas & ice planets



- Molten metallic rocky core
- Liquid iron core

↓

Active interior
Core erosion

Super-Earths

- Solid insulating thermally well conductive rocky mantle
- Solid iron core

↓

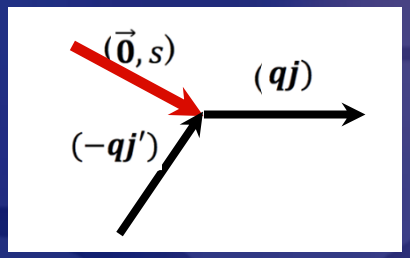
Less active interior

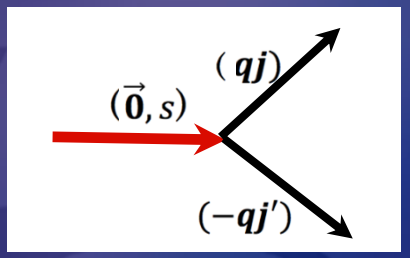
EHIME UNIVERSITY
GRC
GEODYNAMICS RESEARCH CENTER

EHIME UNIVERSITY
GRC
GEODYNAMICS RESEARCH CENTER

Lattice thermal conductivity (Higher order anharmonic lattice dynamics)

$$\kappa = \frac{1}{3}\sum_{s}^{3n}\int \mathbf{v}_{\mathbf{q},s}^{2} c_{\mathbf{q},s}\tau_{\mathbf{q},s} d\mathbf{q}$$





Anharmonic phonon

Phonon lifetime

$$\tau_{\mathbf{q},s} = \frac{1}{2\Gamma(\omega_{\mathbf{q},s})}$$

Bose-Einstein function

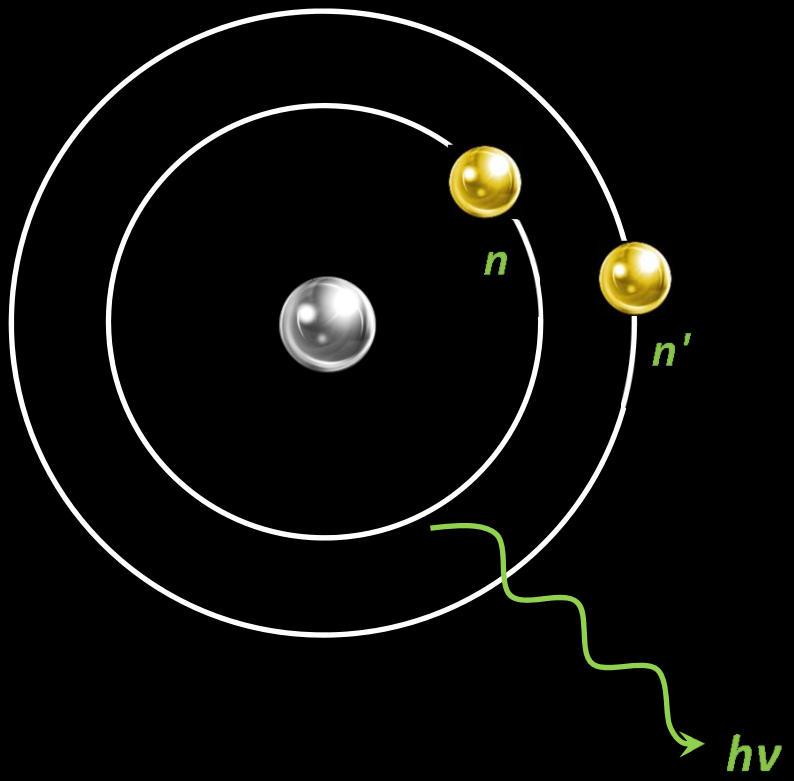
$$n_{\mathbf{q}j} = \frac{1}{e^{\hbar\omega_{\mathbf{q}j}/k_B T} - 1}$$

Phonon damping function

$$\Gamma_{\mathbf{q}j}(\omega) = \frac{\pi}{2}\sum_{\mathbf{q}',j',j''} |V_3(-\mathbf{q}j, \mathbf{q}'j', \mathbf{q}-\mathbf{q}'j'')|^2 \{[1+n_{\mathbf{q}'j'} + n_{\mathbf{q}-\mathbf{q}'j''}]\delta(\omega_{\mathbf{q}'j'} + \omega_{\mathbf{q}-\mathbf{q}'j''} - \omega) + 2[n_{\mathbf{q}-\mathbf{q}'j''} - n_{\mathbf{q}'j'}]\delta(\omega_{\mathbf{q}'j'} - \omega_{\mathbf{q}-\mathbf{q}'j''} - \omega)\}.$$

***V_3*: anharmonic coupling coefficient**

Bohr-Sommerfeld quantization condition



$$\nu \propto \frac{1}{n^2} - \frac{1}{n'^2}$$

$$l = m_e v r = n\hbar$$

$n = 1,2,3, \ldots$

$\hbar$: Plank constant

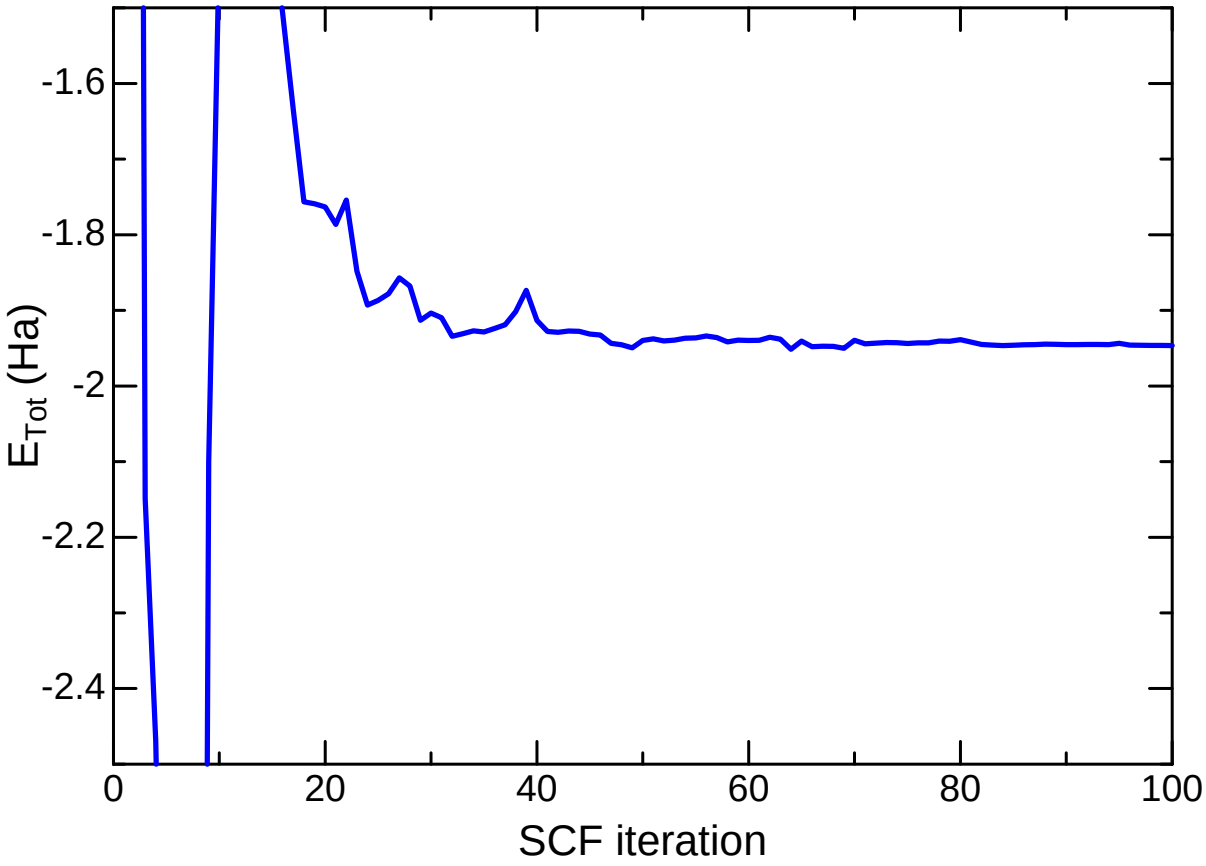
l is discrete, not constant.

$$\oint p dq = n\hbar$$

Quantization condition

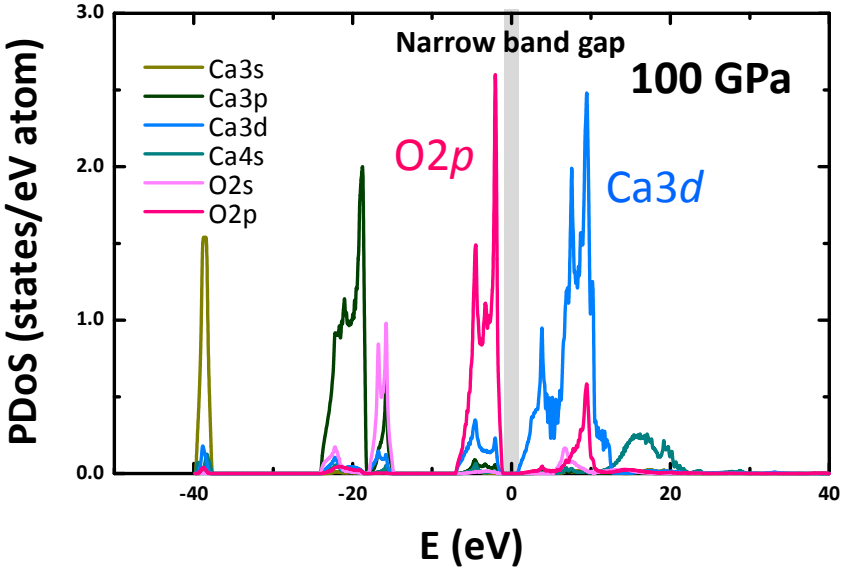
SCF cycle vs total energy variation

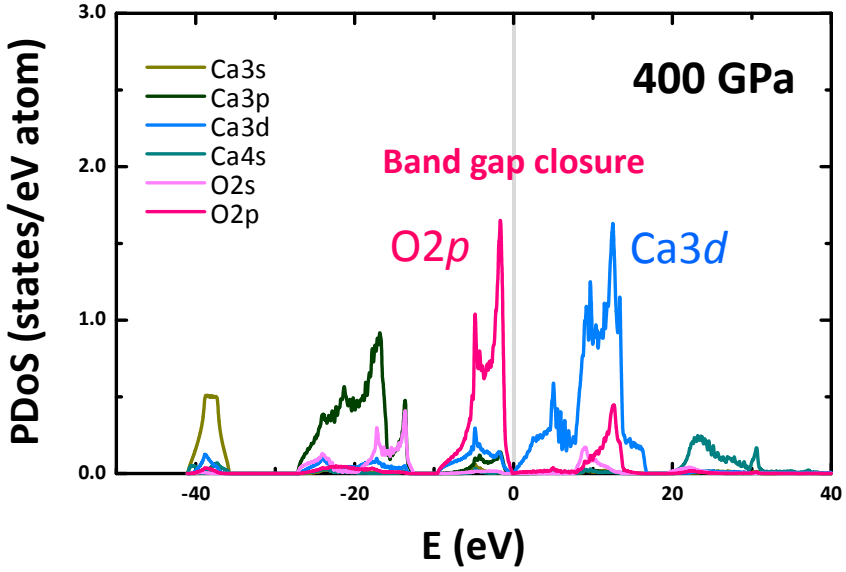
Au fcc structure

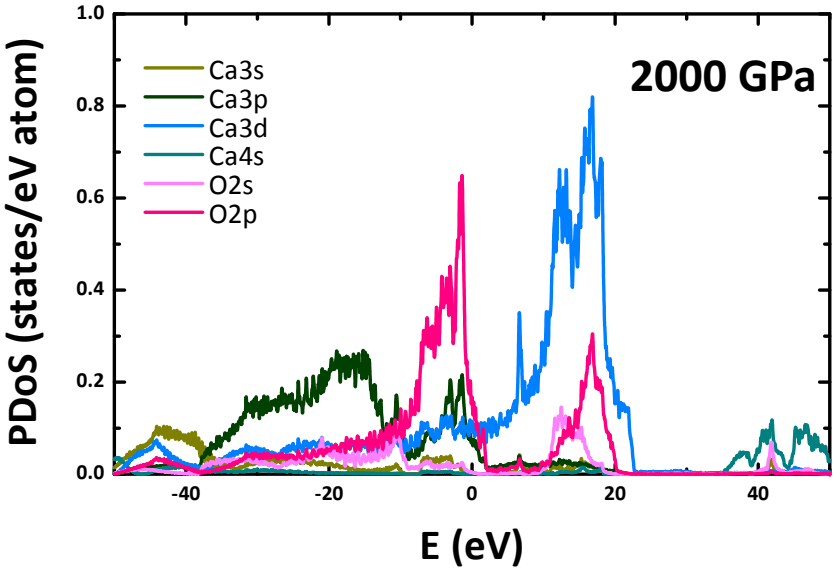


B2-CaO electronic DoS

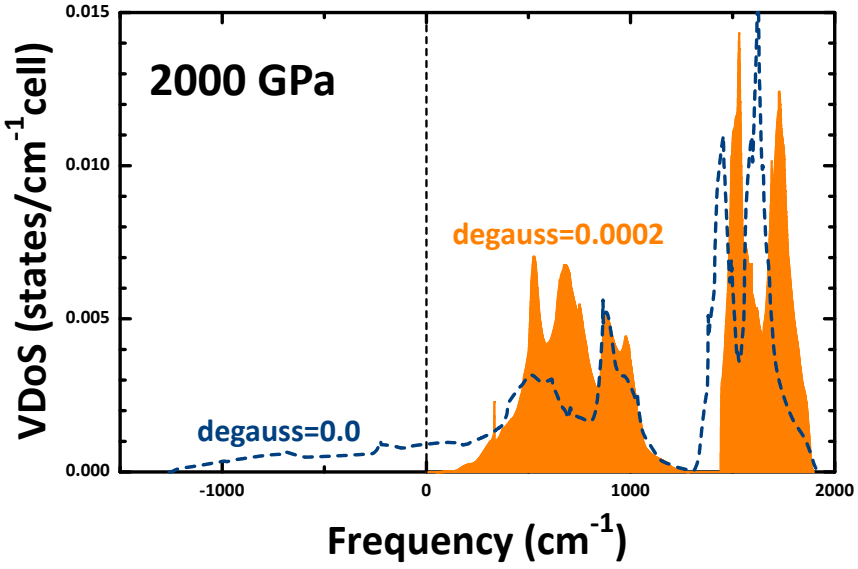
Tsuchiya & Tsuchiya (2011)



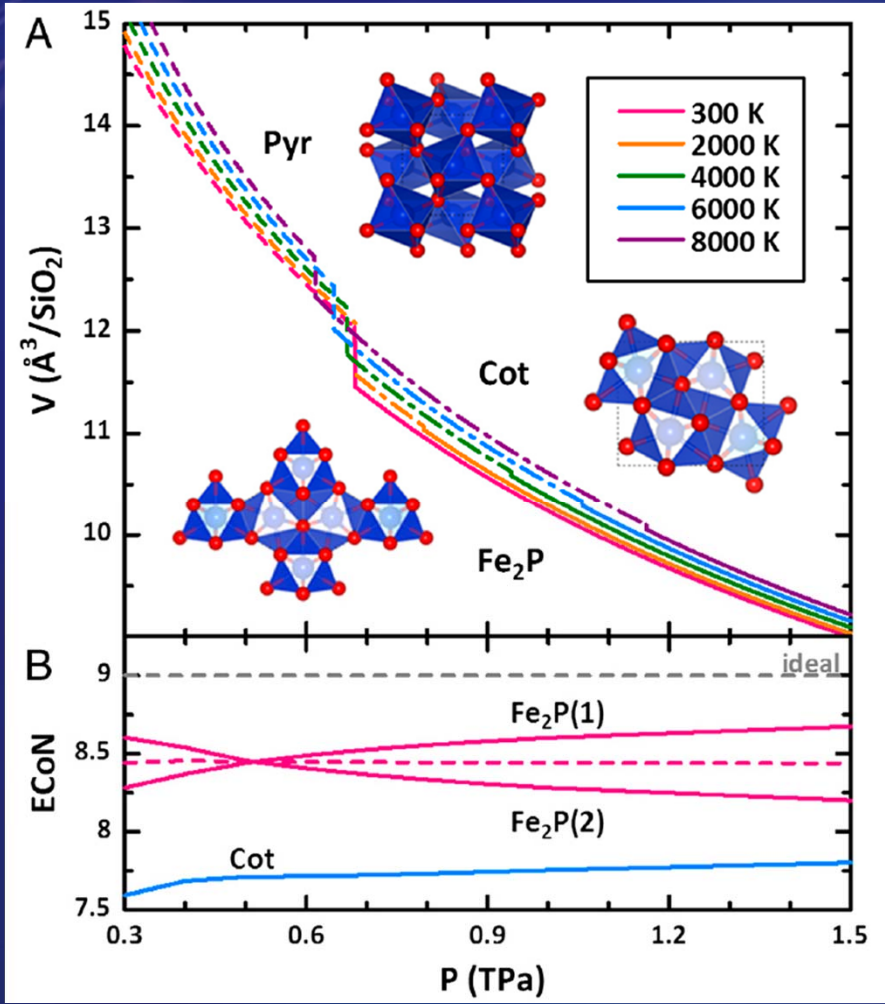




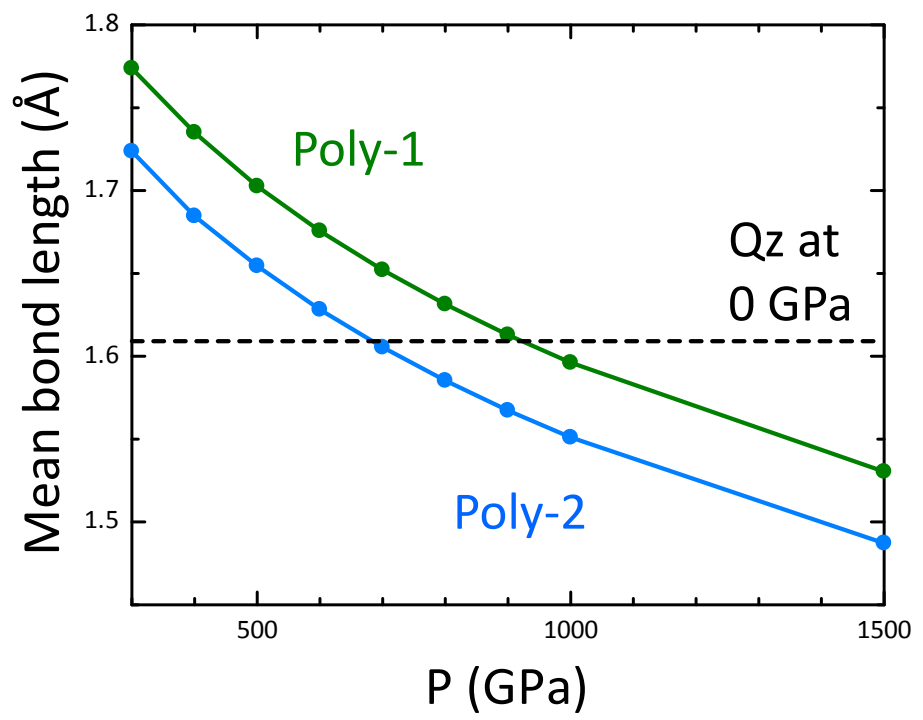
B2-CaO Vibrational DoS



Compression behaviors



Volume



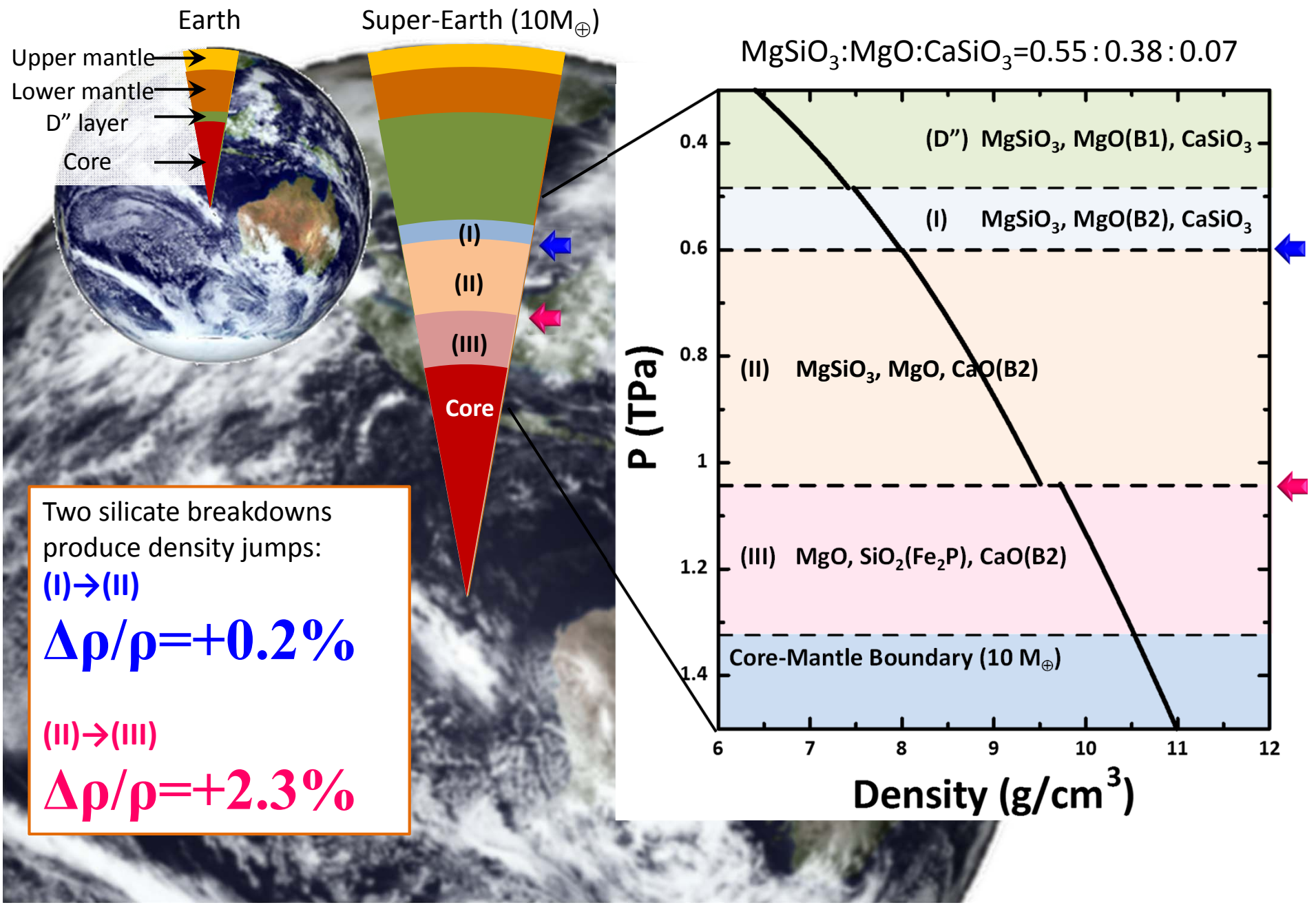
Mean bond lengths in Fe_2P

$$V_{Fe_2P}^{700\ GPa} \sim 0.33 V_{Qz}^{0\ GPa}$$

But the Si-O distance in Fe_2P **comparable to** in Qz even at 1 TPa!!!

Tsuchiya & Tsuchiya (2011) PNAS

Density variation of super-Earth with assuming pyrolitic composition



Periodic boundary condition for a crystal

$$\phi\,(x+a) = \phi\,(x)$$

$$Ga = \pm 2n\pi \;\; (n = 0, 1, 2, 3, \cdots)$$

$$G = 0, \pm\frac{2\pi}{a}, \pm\frac{4\pi}{a}, \cdots, \pm\frac{2n\pi}{a}$$

3-dimensional $\mathbf{G}_\alpha = \pm\frac{2n\pi}{\Omega}(\mathbf{a}_\beta \times \mathbf{a}_\gamma)$

Reciprocal lattice vector

第一原理電子状態計算の限界

①バンドギャップ問題： バンドギャップを過小評価

$$E_{gap}^{LDA} \sim 0.5 E_{gap}^{\exp}$$

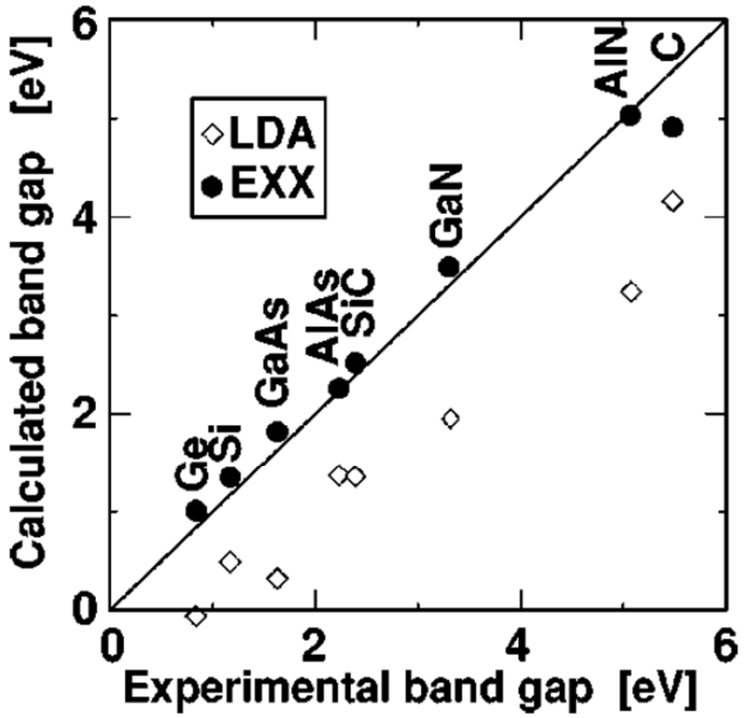


FIG. 3. Comparison of self-consistently calculated LDA and EXX band gaps (in eV) of various semiconductors with experimental data from Refs. 73 and 89–91.

Stadele+ (1999) PRB

②弱い結合： 例）LDA結合距離を過小評価（overbind）

TABLE I. Properties of Bernal-Fowler ice.

	Volume ($Å^3$)	Error (%)	Bulk Modulus (GPa)	Error (%)	Sublimation Energy (eV)	Error (%)
LDA	26.43	−18	25.3	+132	0.99	+71
BP86	30.85	−4	13.5	+24	0.68	+17
PW91	31.35	−2	13.5	+24	0.55	−4
PBE	31.82	−1	12.8	+17	0.53	−8
B-Loc.	39	+22	4	−63	0.24	−42
Exp.	32.05[a]		10.9[b]		0.58[c]	

勾配補正（GGA）

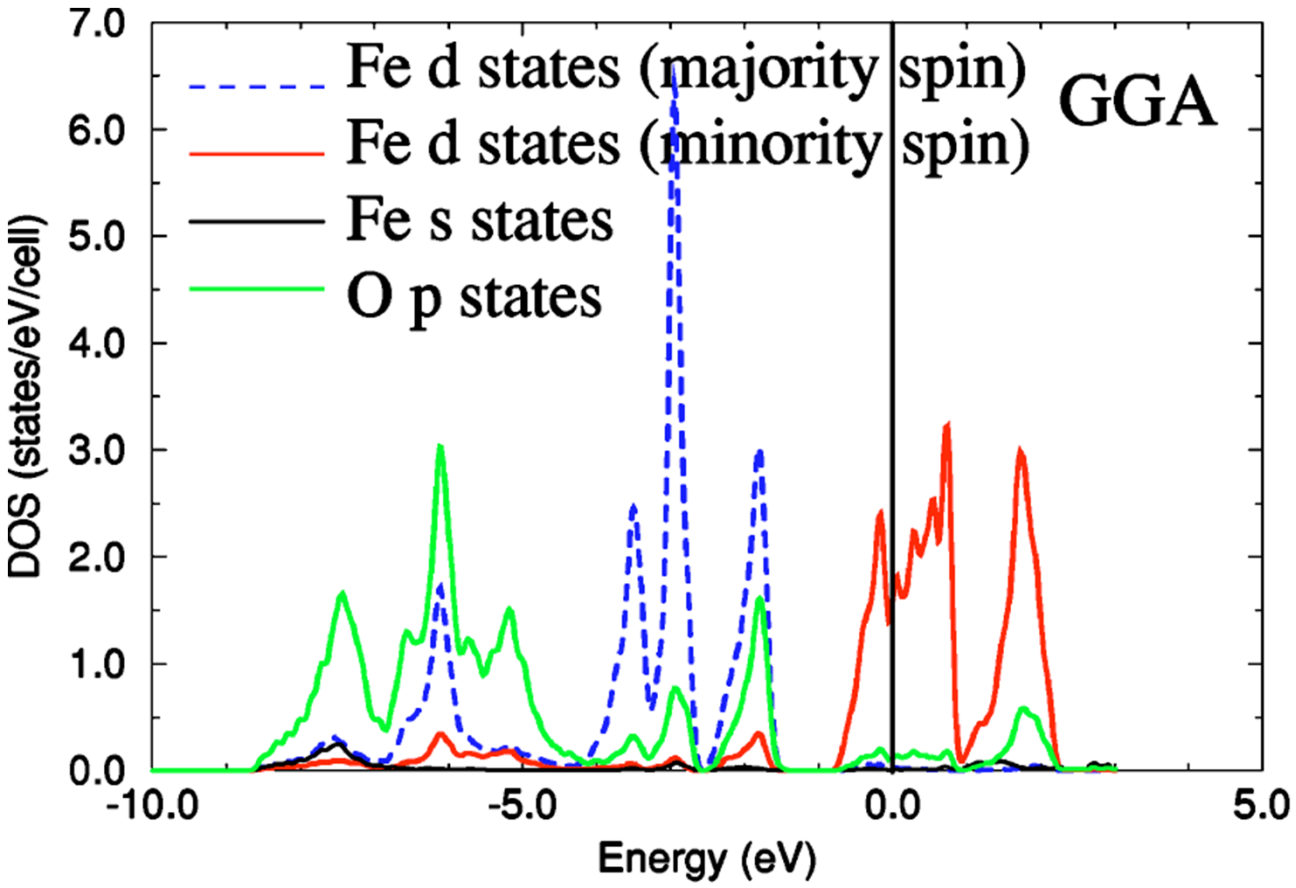
Hamann+ (1997) PRB

GGAにより大きく改善

③遷移金属酸化物の基底状態（強相関電子状態）

例）FeO

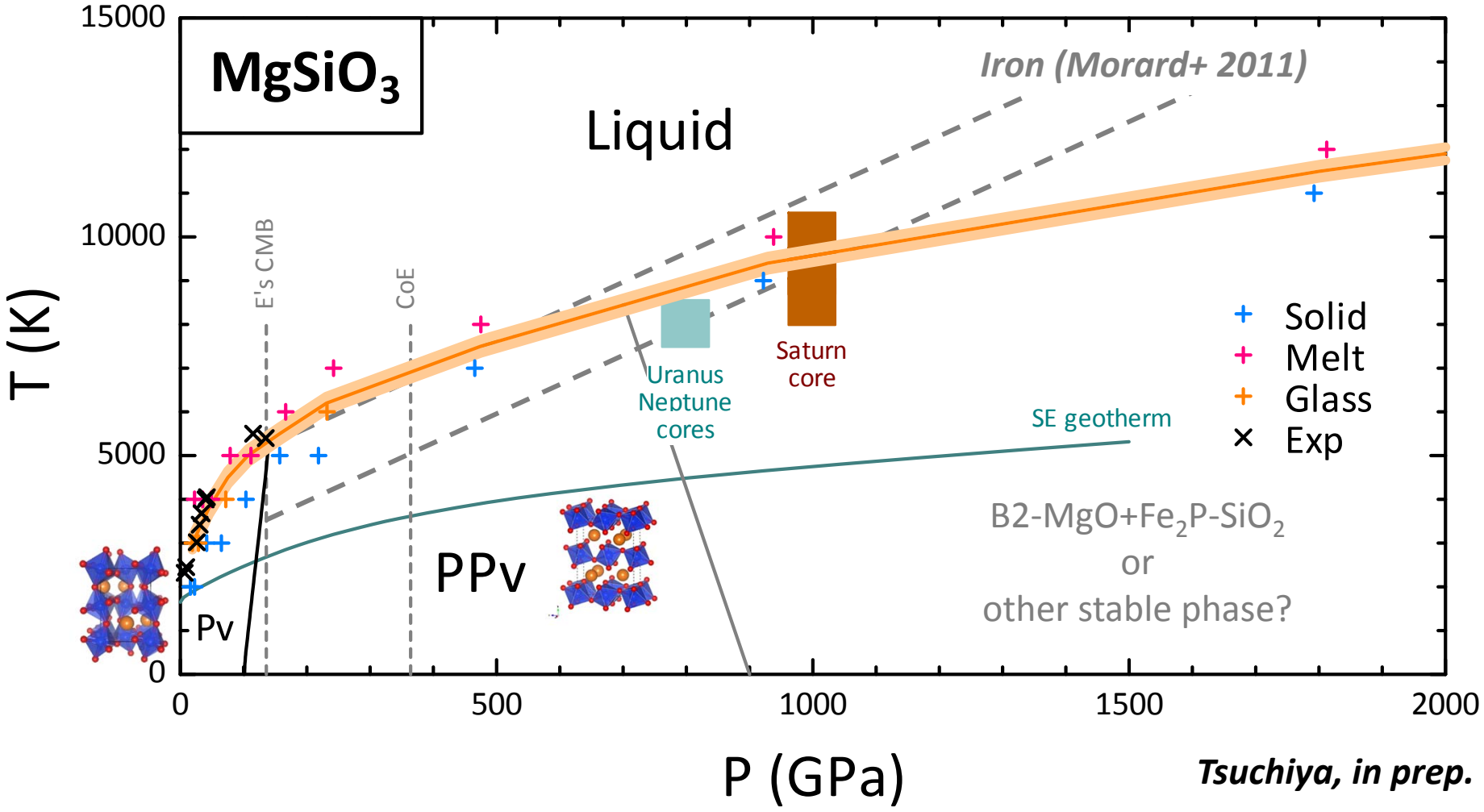
金属電子状態



Cococcioni & de Gironcoli (2005) PRB

実際の絶縁基底状態（E_g～2eV）が再現されない！

Melting curve of $MgSiO_3$



Comparable to the SiO_2's T_M *and also Fe's* T_M

Study on the ultrahigh-pressure phases of Earth and planetary materials

- Just started and now rapidly progressing
- Unexpected phases are continuously discovered. There would still be many other unrevealed structures.
- Off-Hugoniot laser shock appears quite important to confirm calculations experimentally, maybe a unique technique from the experimental side.

Large scale computation

GRC-SRFC parallel cluster systems

Pyrope

Knorringite1,2

愛媛大	土屋 卓久
大阪府立大	上杉 徳照
京大	遠山 貴巳　原田 健自　森成 隆夫

World fastest

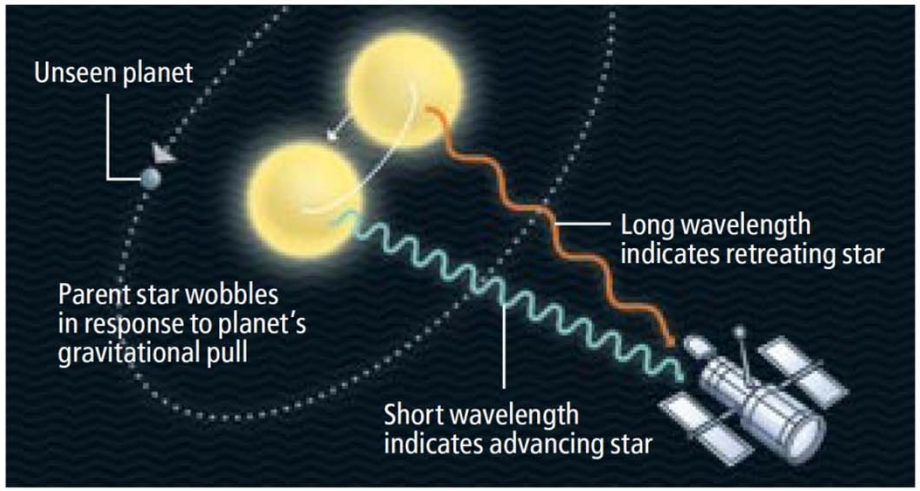
Observation of exsoplanets

Doppler method

Gravitational interaction between a parent star and a planet

↓

- Existence of a planet
  - **Mass** of a planet

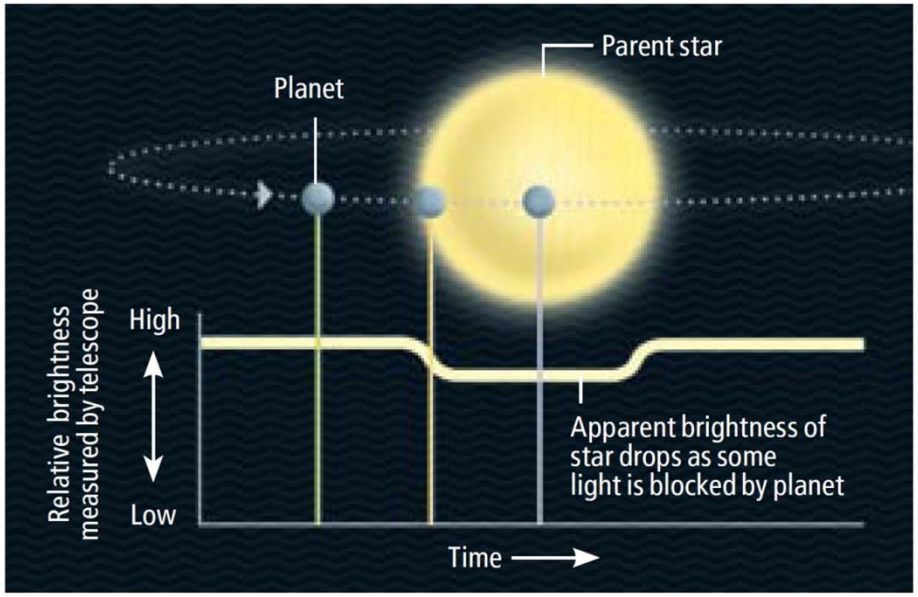


Transit method

Eclipse by a planet, i.e., the light of a parent star dimmed by a transiting planet

↓

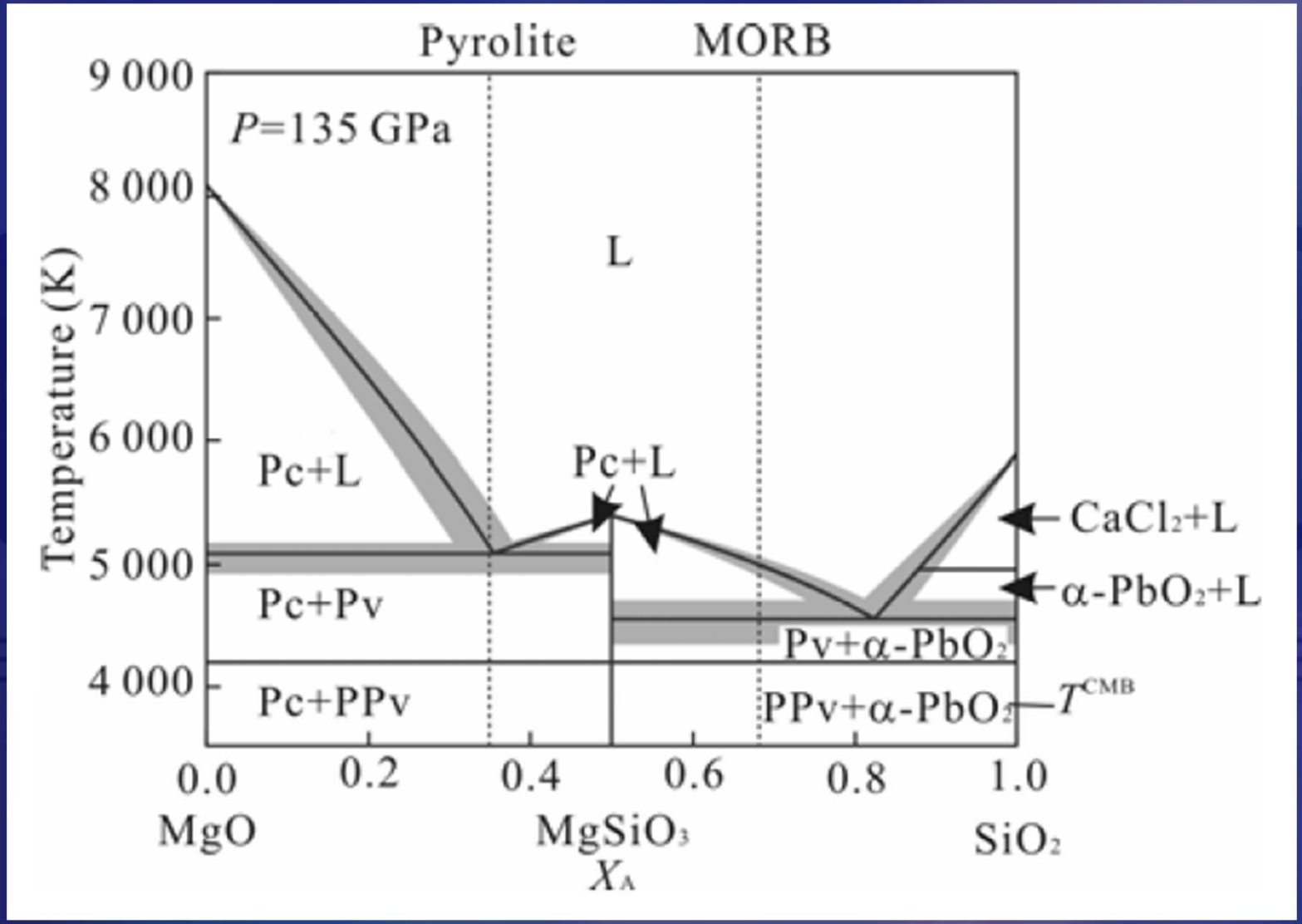
- Existence of a planet
  - **Size** of a planet



Mass + Size ⇒ Mean density

Sasselov (2008)

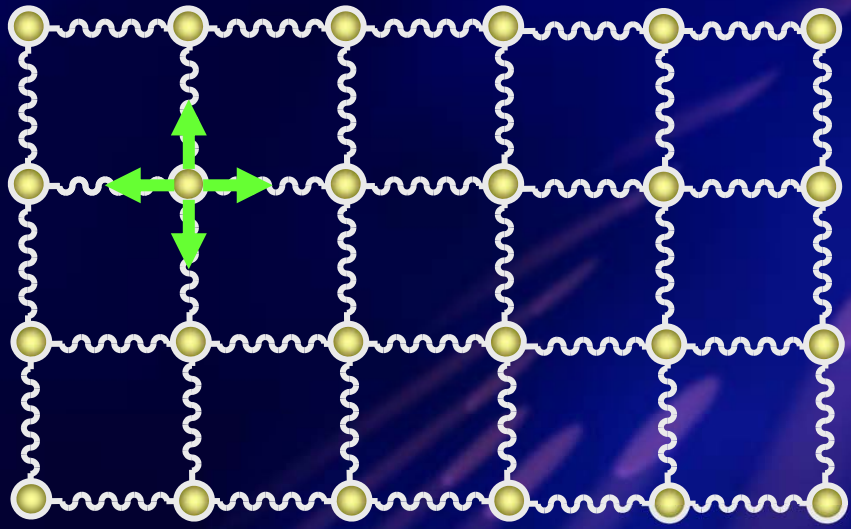
Eutectic melting relation in the MgO-SiO_2 system

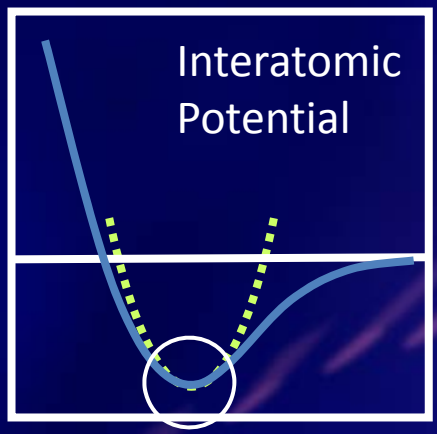


Lattice Dynamics method

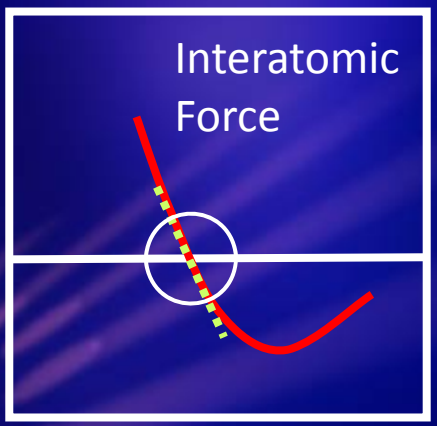
Atomic thermal vibration in sold

⇒ Collective motion of oscillators (phonon)





Harmonic Approximation
$\Delta E=(k/2)\Delta x^2$



Linear Approximation
$F=-k\Delta x$

Dynamical matrix

$$D^{\alpha\beta}_{\kappa\kappa'}(\mathbf{q}) = \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \sum_l \Phi^{\alpha\beta}_{\kappa\kappa'}(0l)\exp\{-i\mathbf{q}\cdot(\mathbf{x}_0 - \mathbf{x}_l)\}$$

Harmonic force constant matrix

Phonon dispersion relation

A milestone from K (November/2011):

First-principles calculations of electron states of a silicon nanowire

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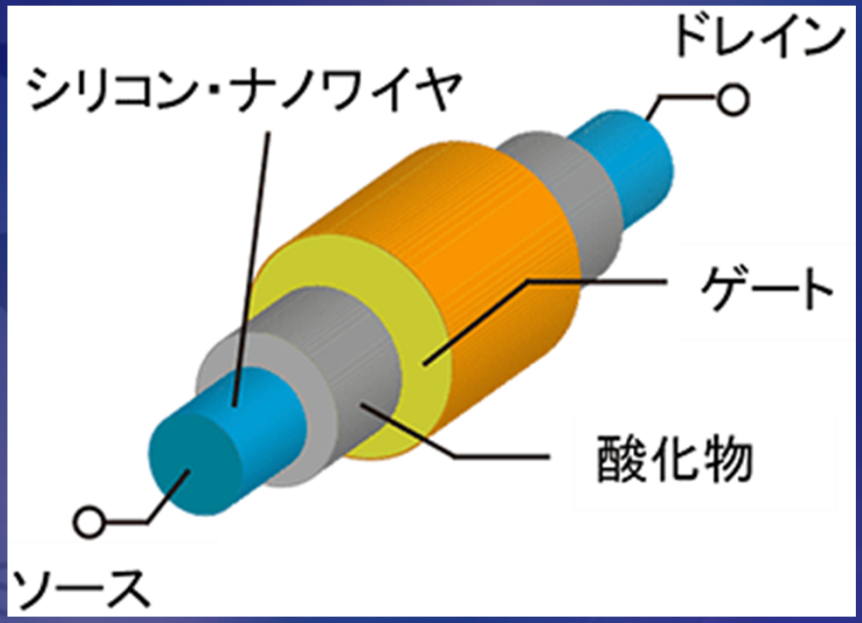
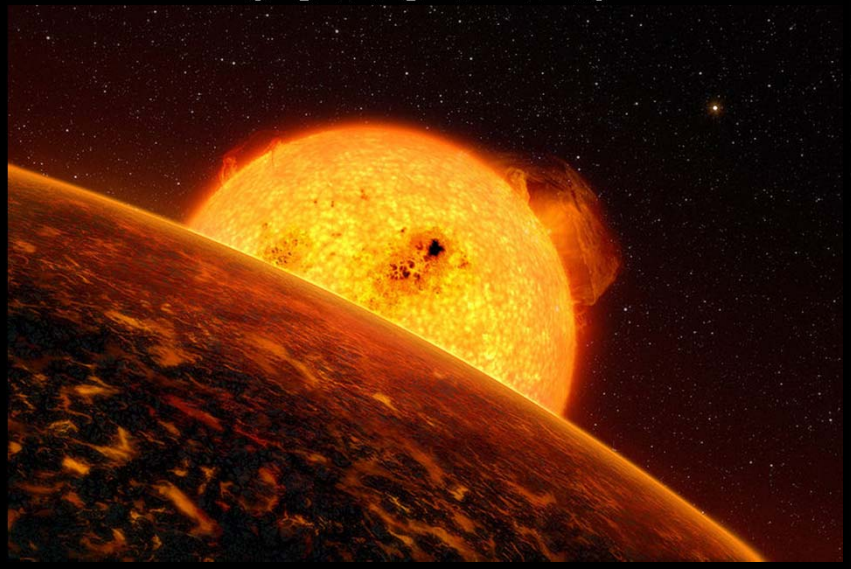


100,000 atoms!!!

Calculations with a few hundred atoms now not special

Examples of the transit planet

CoRoT-7b



Discovery: 2009

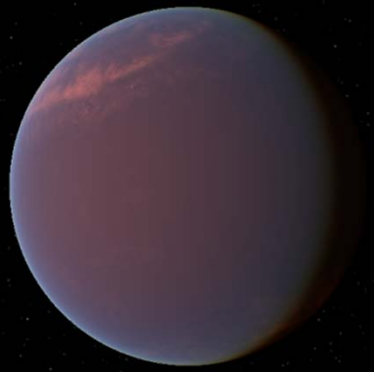
$M = \sim 4.8\ M_{\oplus}$

$R = \sim 1.7\ R_{\oplus}$

$\langle \rho \rangle = \sim 5.6\ \mathrm{g/cm^3} \sim \langle \rho_{\oplus} \rangle$

Rocky

GJ1214b



Discovery: 2009

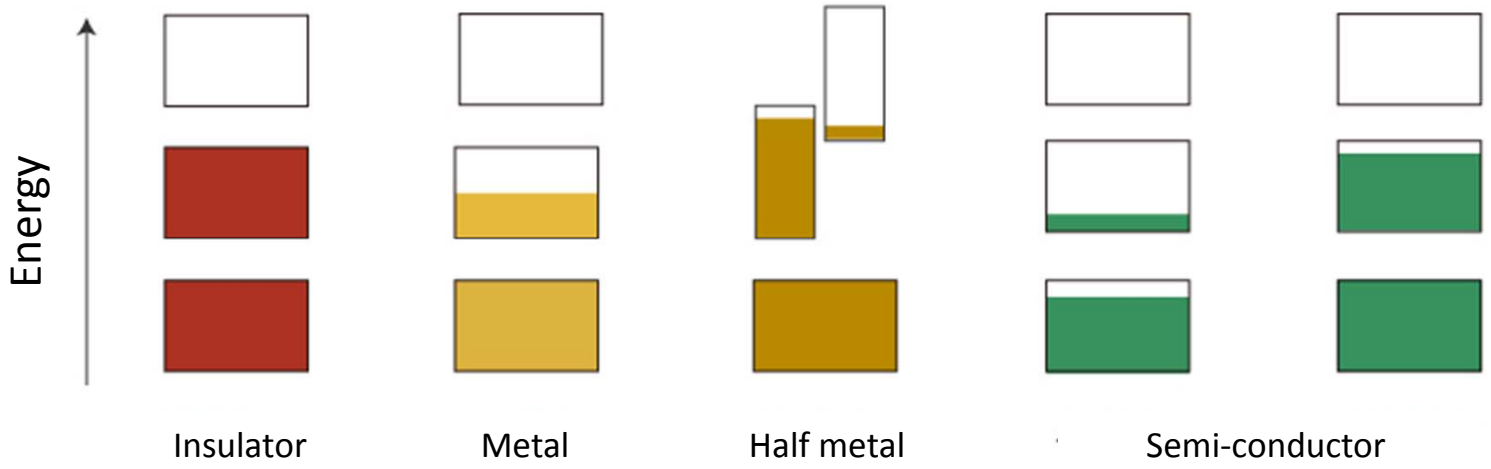
$M = \sim 6.55\ M_{\oplus}$

$R = \sim 2.7\ R_{\oplus}$

$\langle \rho \rangle = \sim 1.9\ \mathrm{g/cm^3} < \langle \rho_{\oplus} \rangle$

Icy

Electronic structure of solids

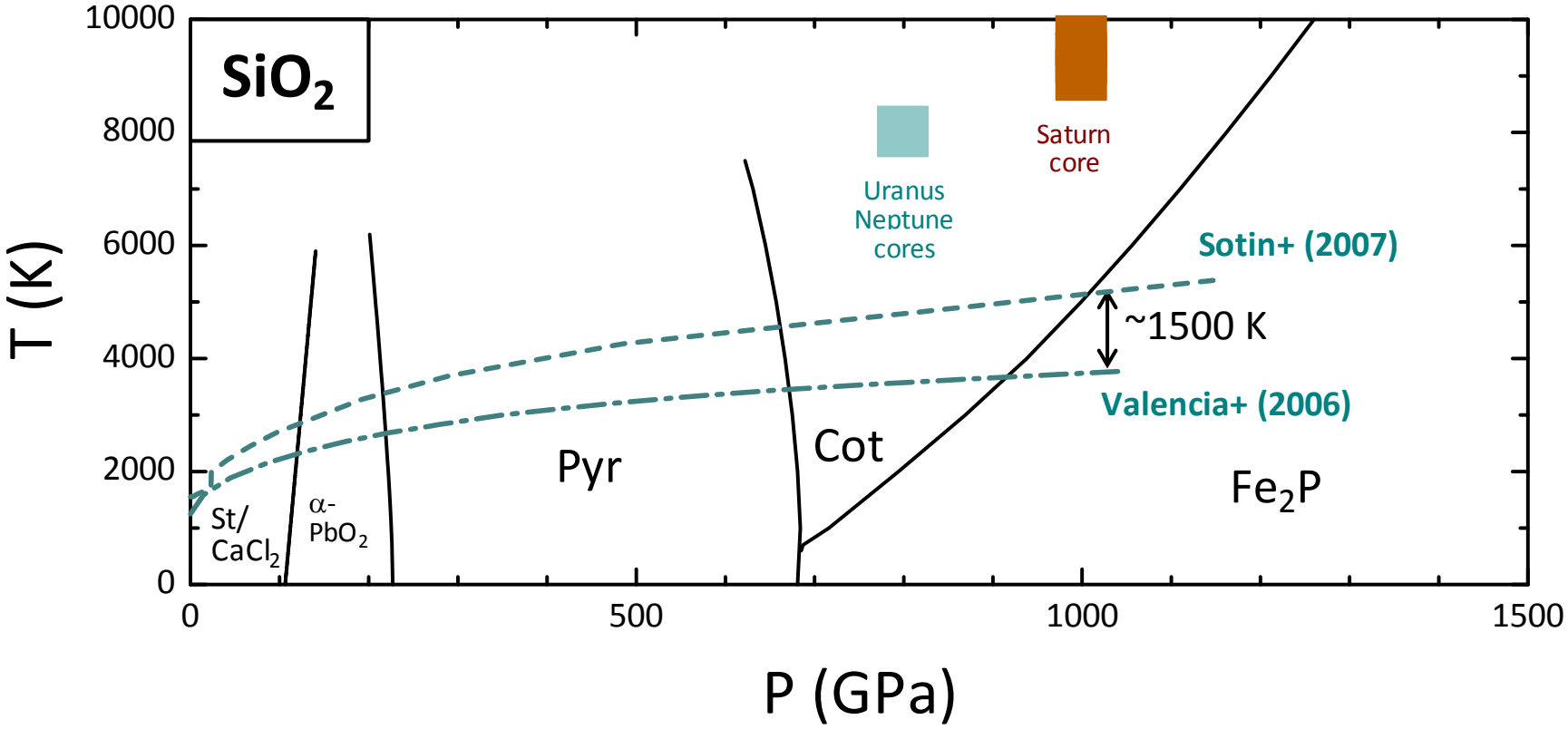


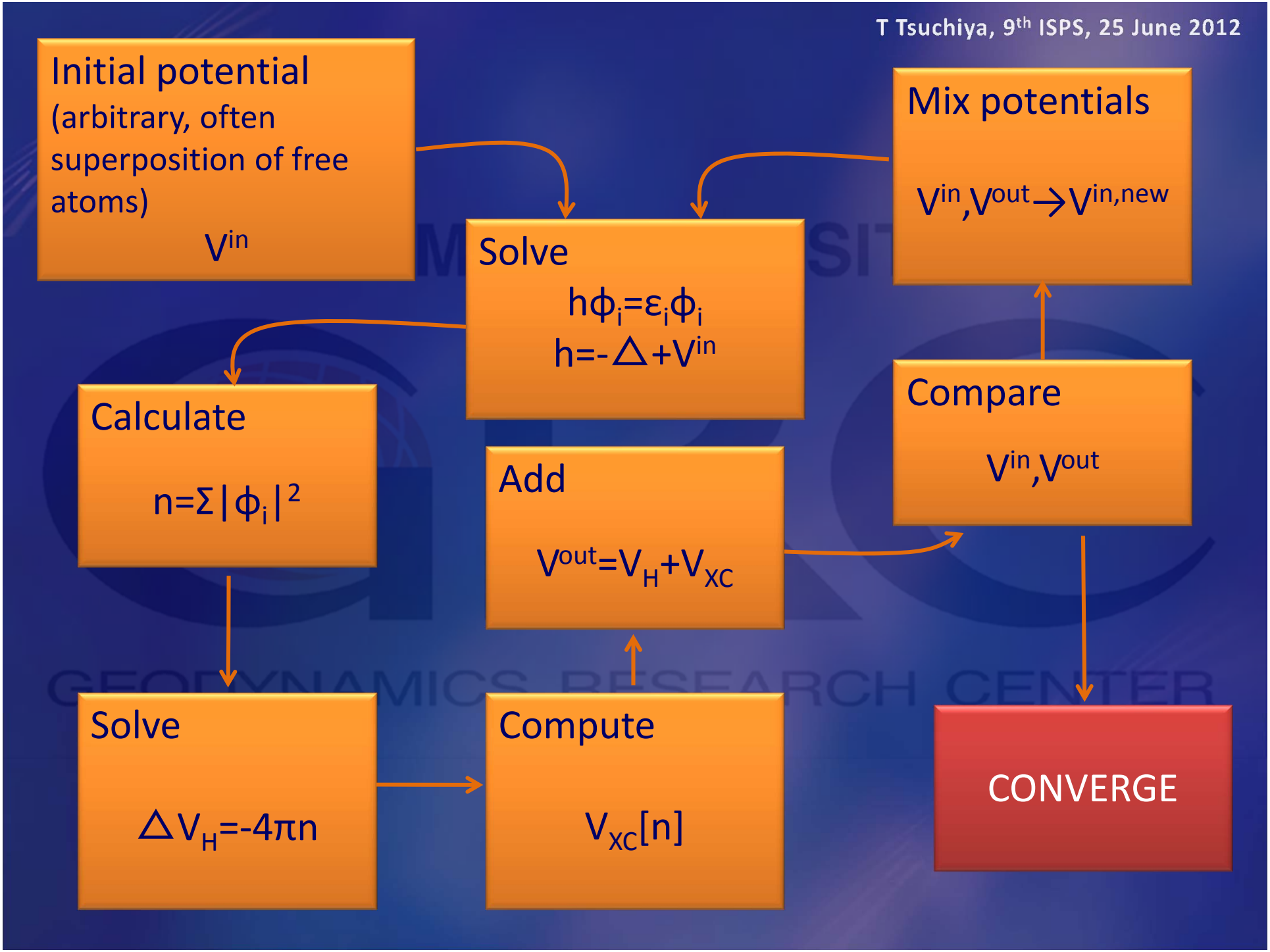
Electronic state distribution

Thermal structure of SE

Adiabatic temperature gradient

$$\left(\frac{dT}{dP}\right)_S = \frac{\alpha(P)g(P)T}{C_P(P)}$$




Initial potential
(arbitrary, often superposition of free atoms)
V^{in}
Solve
$h\phi_i=\varepsilon_i\phi_i$
$h=-\Delta+V^{in}$
Mix potentials
$V^{in},V^{out}\rightarrow V^{in,new}$
Calculate
$n=\Sigma|\phi_i|^2$
Add
$V^{out}=V_H+V_{XC}$
Compare
V^{in},V^{out}
Solve
$\Delta V_H=-4\pi n$
Compute
$V_{XC}[n]$
CONVERGE

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