Ab initio materials properties at extreme conditions

DE-SC0019759, NSF-EAR-1918126, -2000850

PI Renata Wentzcovitch, Applied Physics and Applied Mathematics

COLUMBIA | ENGINEERING
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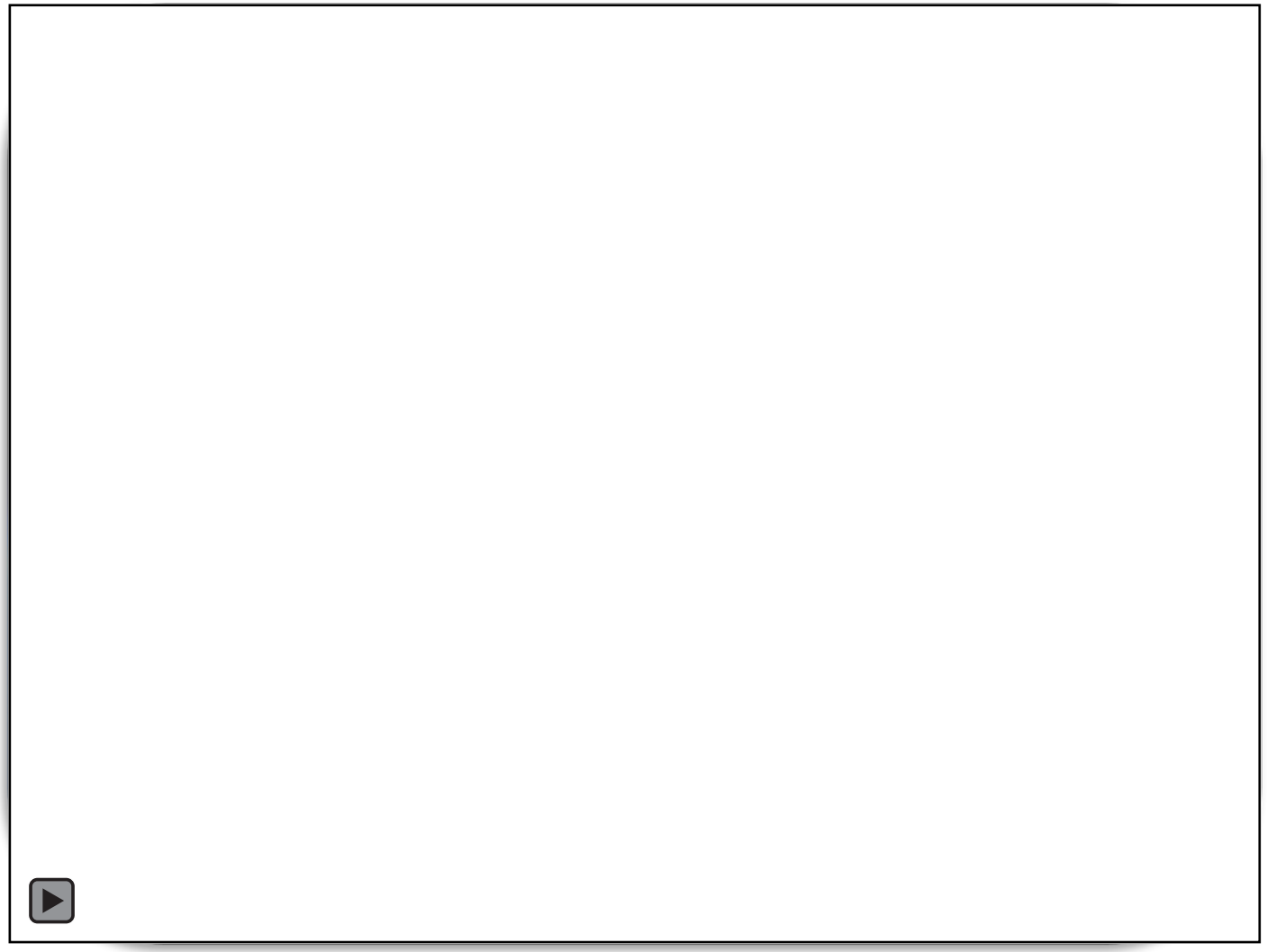
Earth and Environmental Sciences

Lamont-Doherty Earth Observatory
COLUMBIA UNIVERSITY | EARTH INSTITUTE

- **Overview**
- **Goals**
- **Accomplishments**
  - **Software**
  - **Infrastructure**
  - **Databases**
- **Other research going on**

Overview: Cross-scale and interdisciplinary modeling of Earth's interior



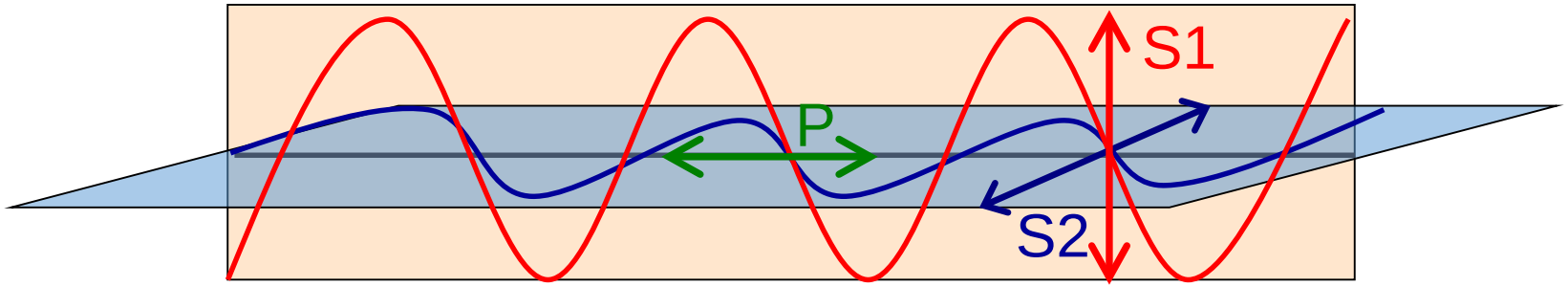
Body wave (acoustic) velocities

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

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

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

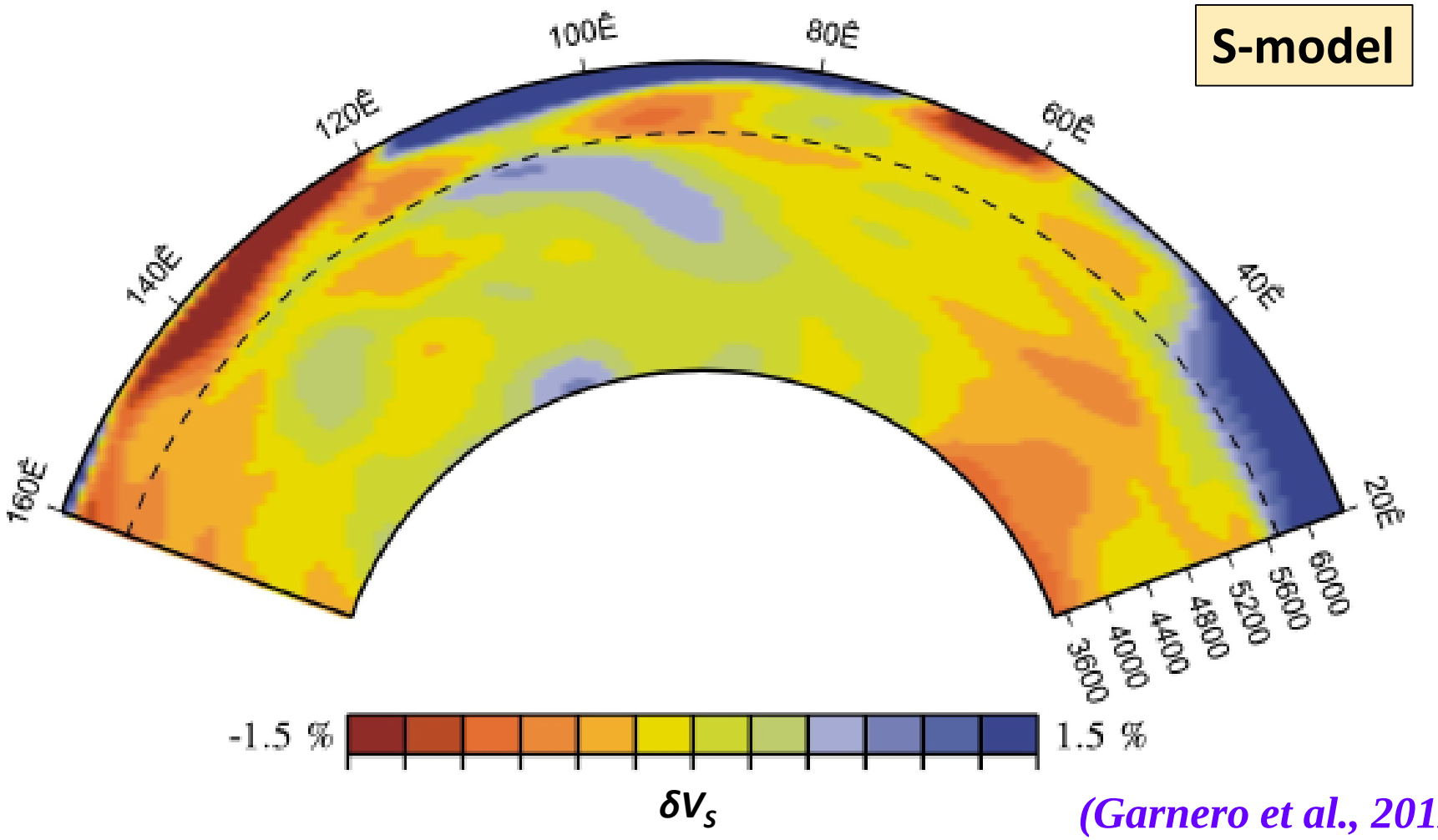
$$V_S = \sqrt{\frac{G}{\rho}}$$



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

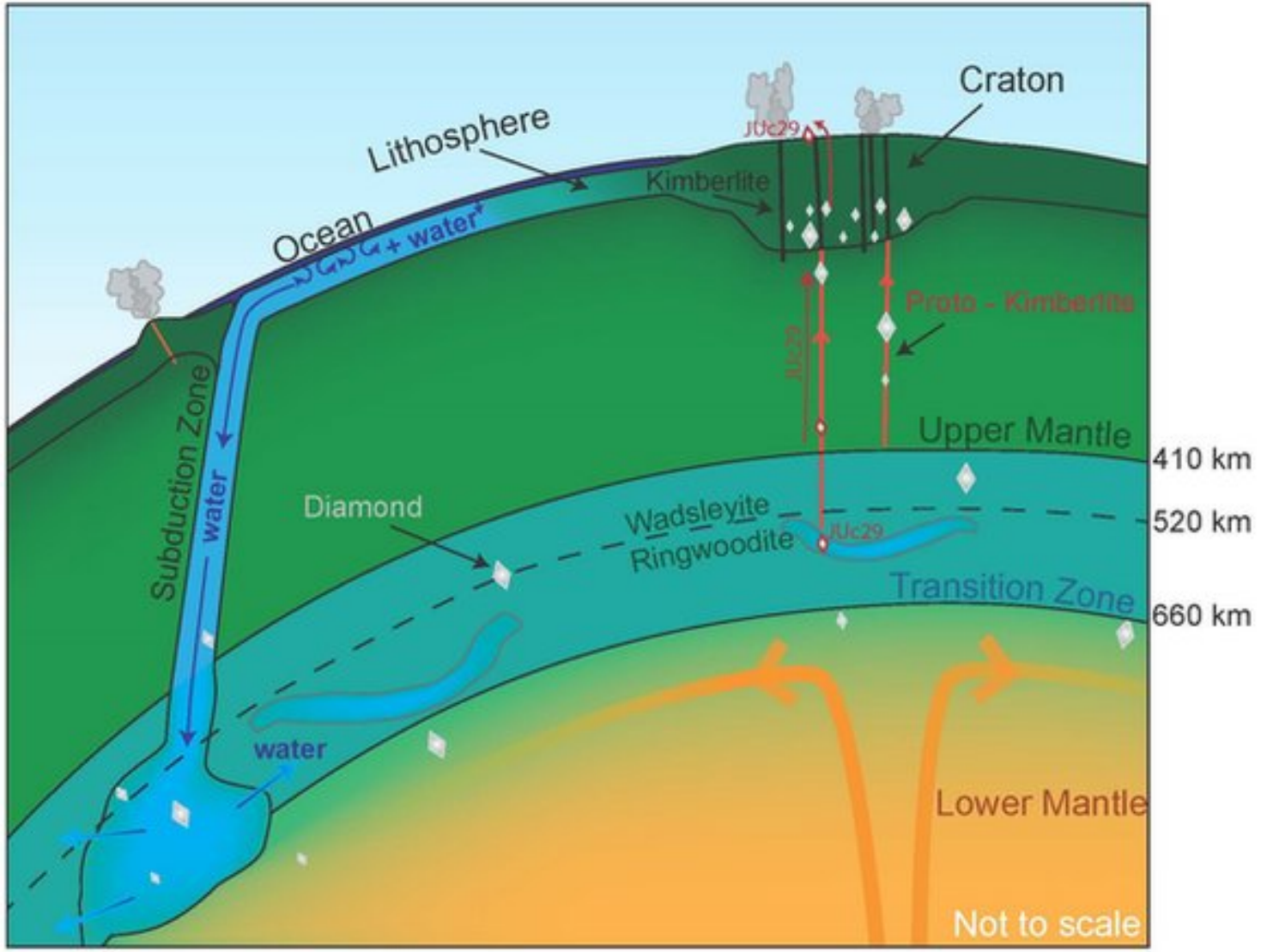
K and ***G*** from Voigt-Reuss-Hill bounds

Making sense of mantle heterogeneities (Seismic Tomography)



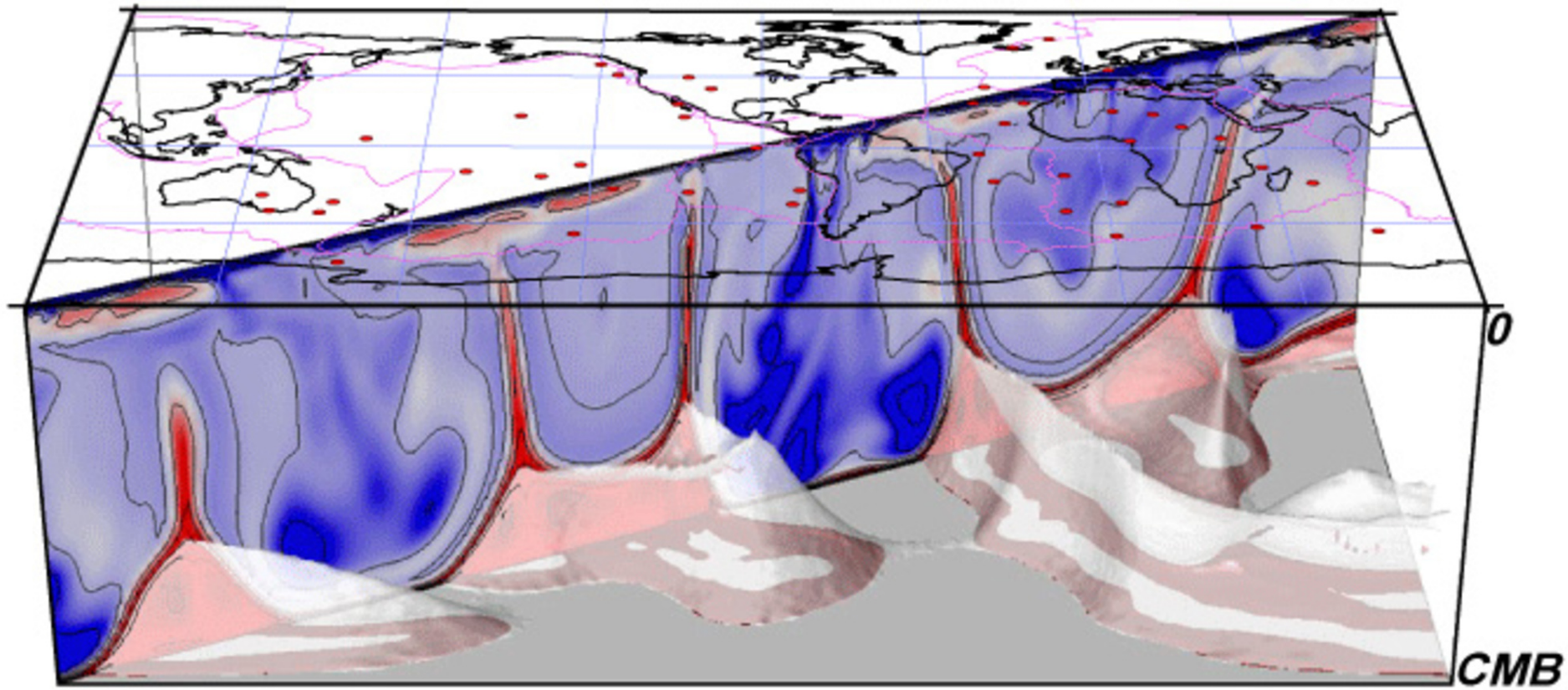
(Garnero et al., 2011)

The Deep Water Cycle



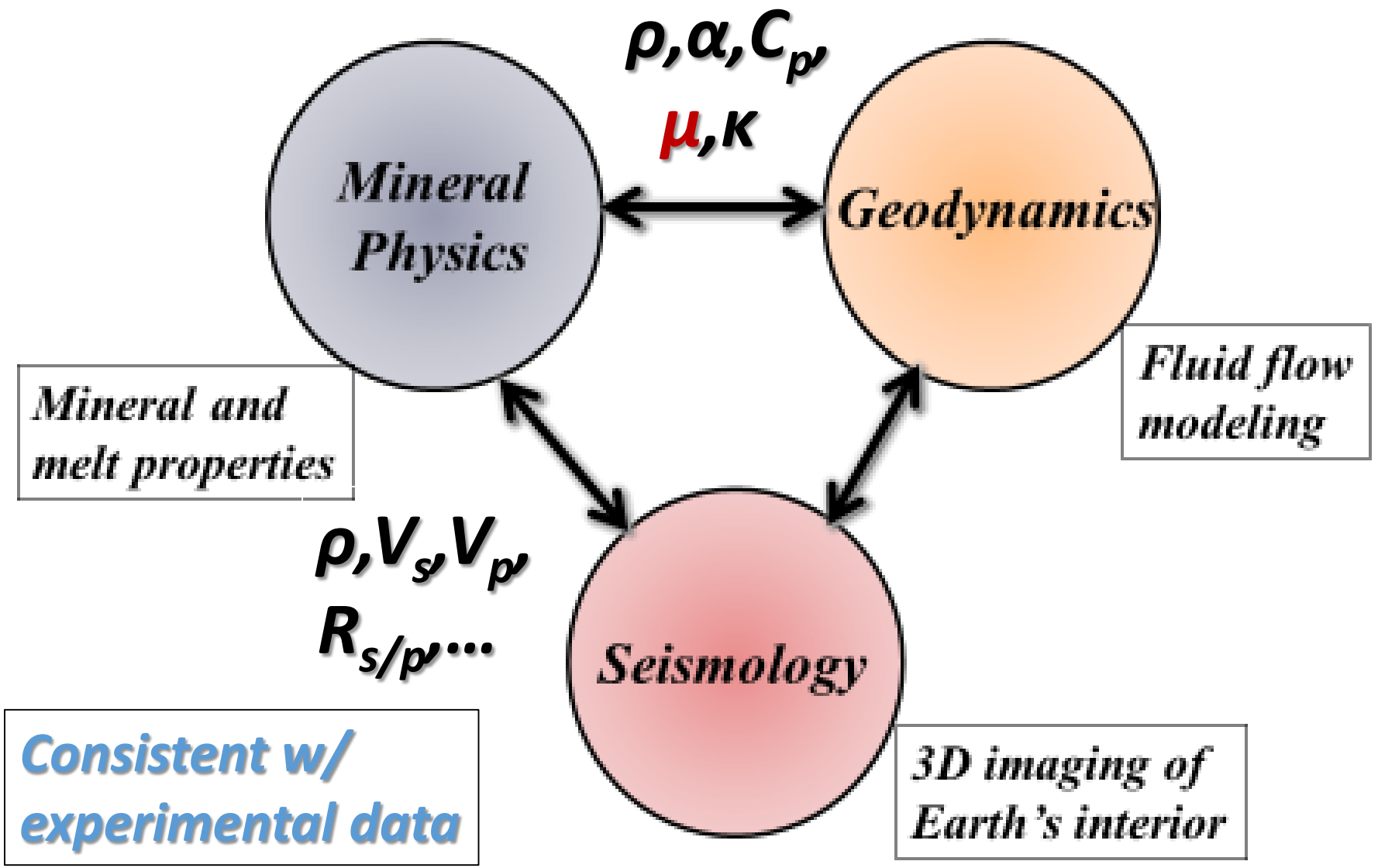
Pearson et al., *Nature* **507**, 221 (2014) DOI: 10.1038/nature13080

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



(McNamara et al., 2014)

Overview: Cross-scale and interdisciplinary modeling of Earth's interior



Goals:

- **Goal #1** – Interpret seismic velocity heterogeneties in terms of temperature and mineralogy
- **Goal #2** - Enable the seismic detection of water in hydrous phases in Earth's interior
- **Goal #3** - Maintain and enhance a computational infrastructure for calculations. It consists of:

  a) methods and software for calculations of relevant properties

  b) workflows to automate long sequences of calculations

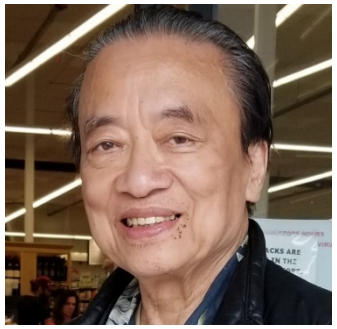
  c) an online database to communicate results

  d) a Web portal where some calculations can be carried out or reproduced

  e) implementation of HPC/HTC calculations in the Oak Ridge leadership computing facility (ORNL-LCF)

Personnel at Columbia University

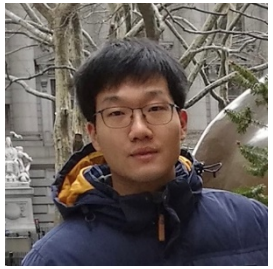
Prof. Renata Wentzcovitch
APAM/DEES
Materials Physics



Dr. David A. Yuen
APAM
Geodynamics

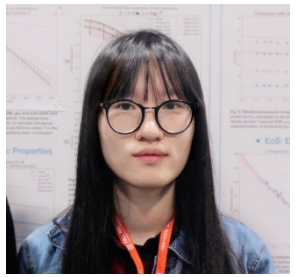
Dr. Pedro da Silveira
APAM and Apple Inc.
Comp. Science

Dr. Yang Sun
APAM
Materials Physics



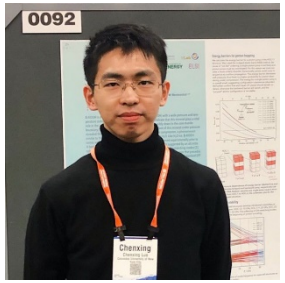
Zhen Zhang
PhD-APAM
(3rd–4th yr)

Qi Zhang
PhD-APAM
(2nd–3rd yr)



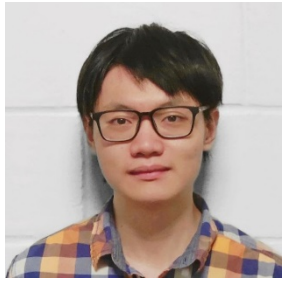
Jingyi Zhuang
PhD-DEES
(1st–2nd yr)

Tianqi Wan
PhD-APAM
(1st–2nd yr)



Chenxing Luo
PhD-APAM
(1st–2nd yr)

Hongjin Wang
MSc-CS
(1st–2nd yr)



Chaoxuan Gu
MSc-APAM
(1st–2nd yr)

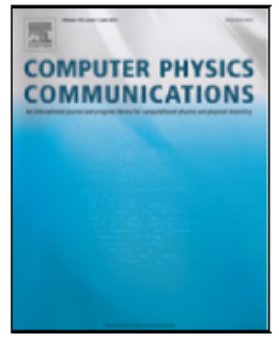
Software for calculation of relevant properties

Computer Physics Communications 237 (2019) 199–207

Contents lists available at ScienceDirect

Computer Physics Communications

journal homepage: www.elsevier.com/locate/cpc



qha: A Python package for quasiharmonic free energy calculation for multi-configuration systems☆

Tian Qin [a,b], Qi Zhang [c], Renata M. Wentzcovitch [b,c,*], Koichiro Umemoto [d]

[a] Department of Earth Sciences, University of Minnesota, 116 Church Street SE, Minneapolis, MN 55455, USA
[b] Lamont-Doherty Earth Observatory, Columbia University in the City of New York, 61 Route 9W, Palisades, NY 10964, USA
[c] Applied Physics and Applied Mathematics Department, Columbia University in the City of New York, 500 W. 120th St., Mudd 200, MC 4701 New York, NY 10027, USA
[d] Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1-IE-12 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

Note: “Phonopy” - QHA for single configuration

Contents lists available at ScienceDirect (2010)

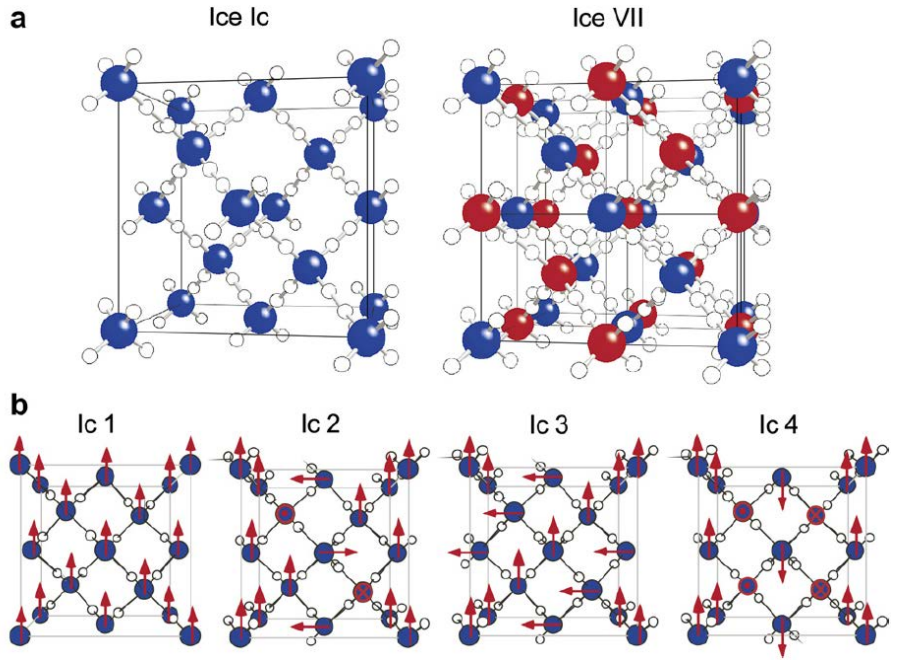
Chemical Physics Letters

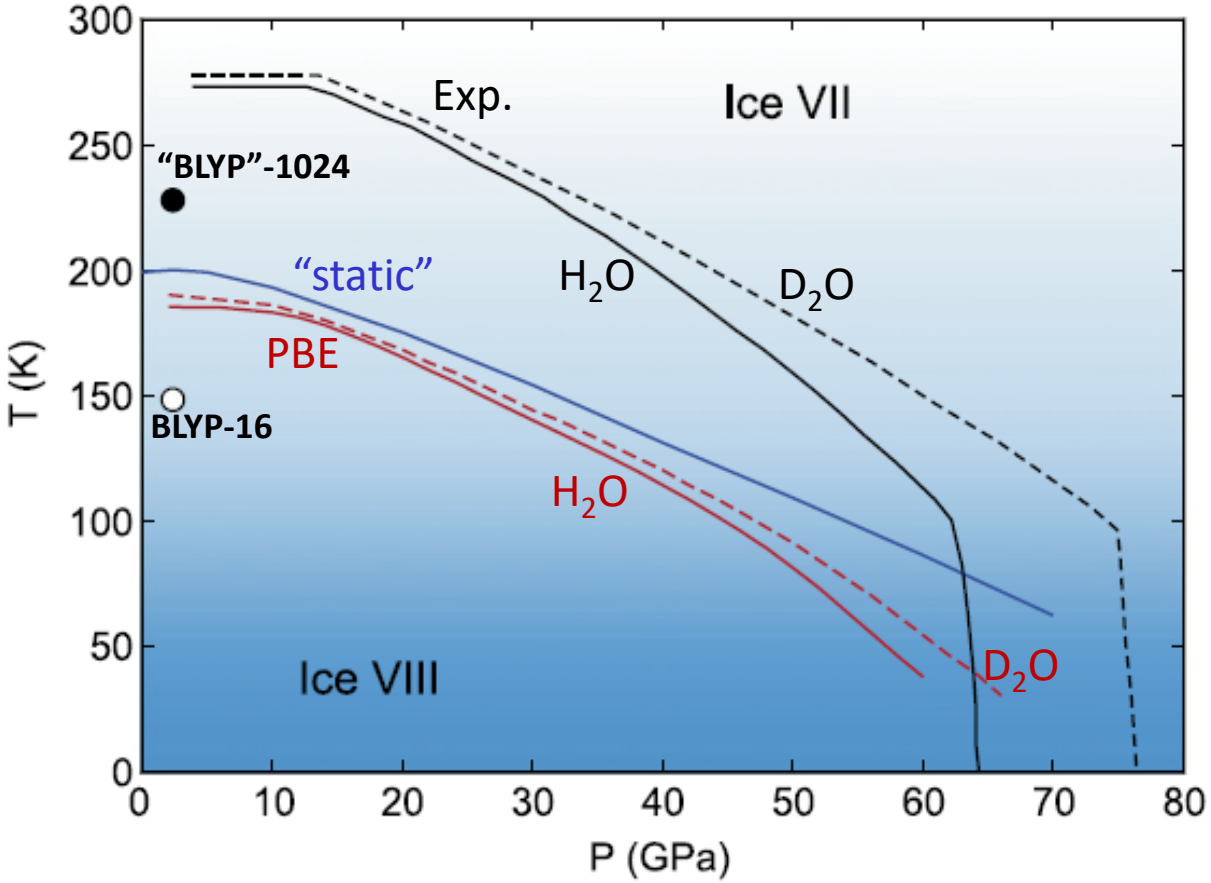
journal homepage: www.elsevier.com/locate/cplett

Order–disorder phase boundary between ice VII and VIII obtained by first principles

Koichiro Umemoto [a,*], Renata M. Wentzcovitch [b], Stefano de Gironcoli [c], Stefano Baroni [c]

Full statistical sampling of H-configurations in
16 molecule/supercell = 8,100 configs. = <u>52 inequivalent configs.</u>



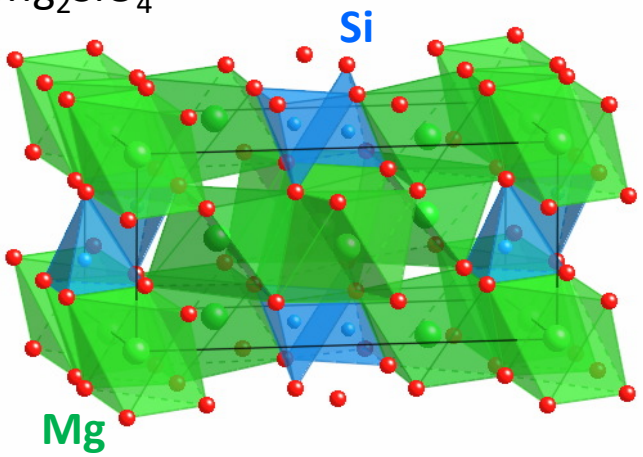


American Mineralogist, Volume 103, pages 692–699, 2018

Ab initio study of water speciation in forsterite: Importance of the entropic effect

TIAN QIN[1,2], RENATA M. WENTZCOVITCH[2,3,*,†], KOICHIRO UMEMOTO[4], MARC M. HIRSCHMANN[1], AND DAVID L. KOHLSTEDT[1]

Mg_2SiO_4



$SiO_2 \rightarrow 2\ H_2O$ (*ab initio*)

or

$MgO \rightarrow H_2O$ (Exp.) **?**

Nominally **A**nhydrous **M**ineral (**NAM**)

American Mineralogist, Volume 103, pages 692–699, 2018

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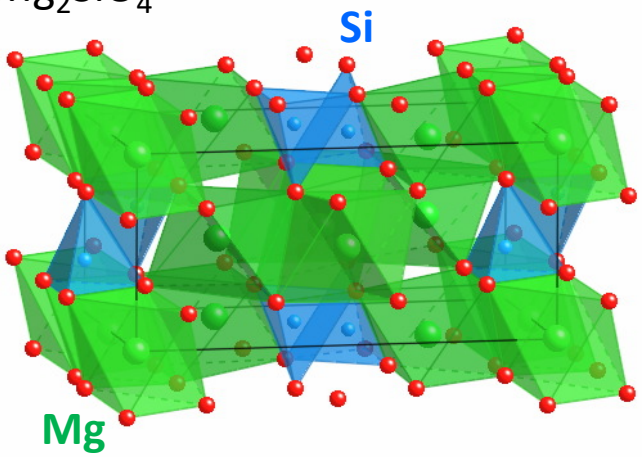

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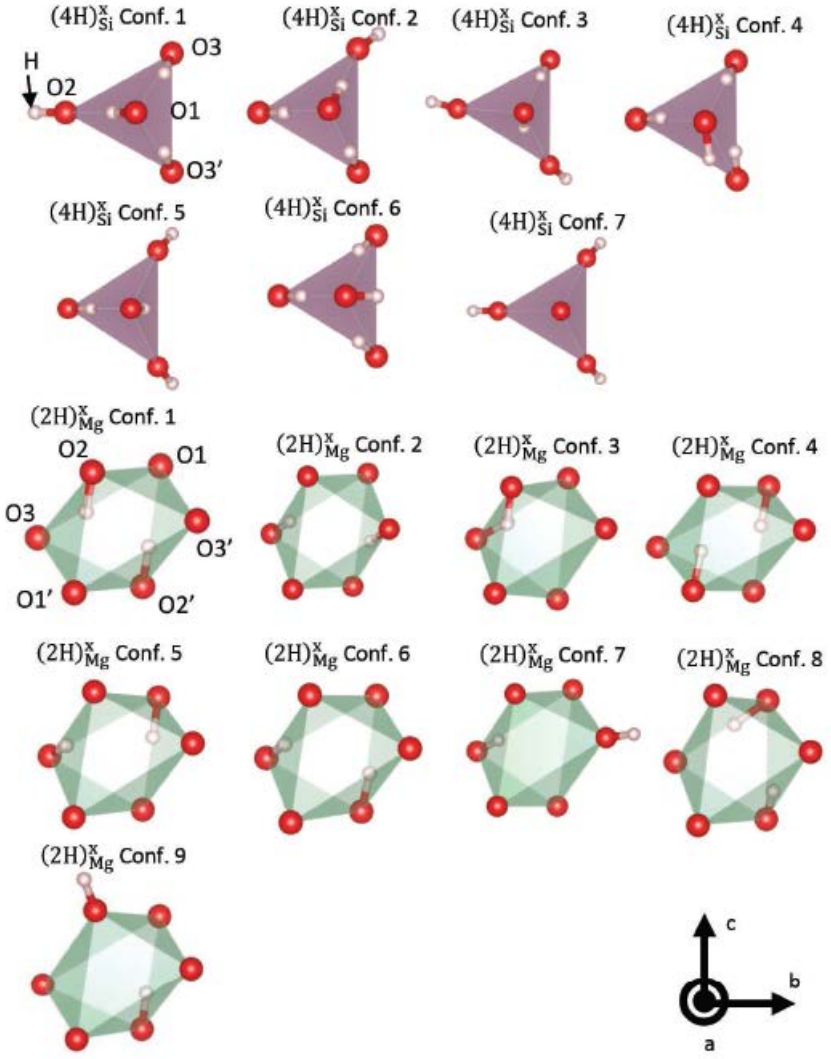

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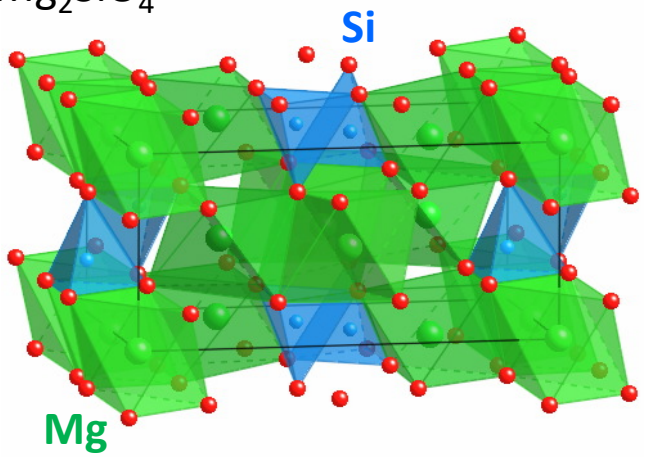

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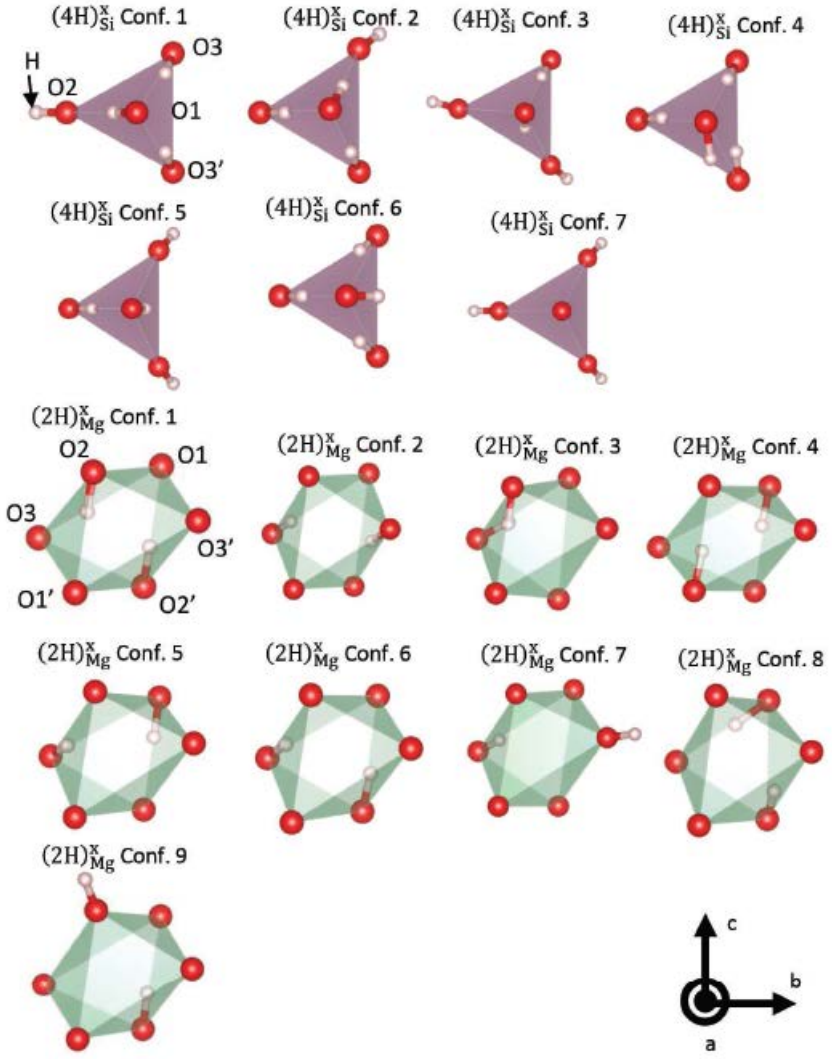

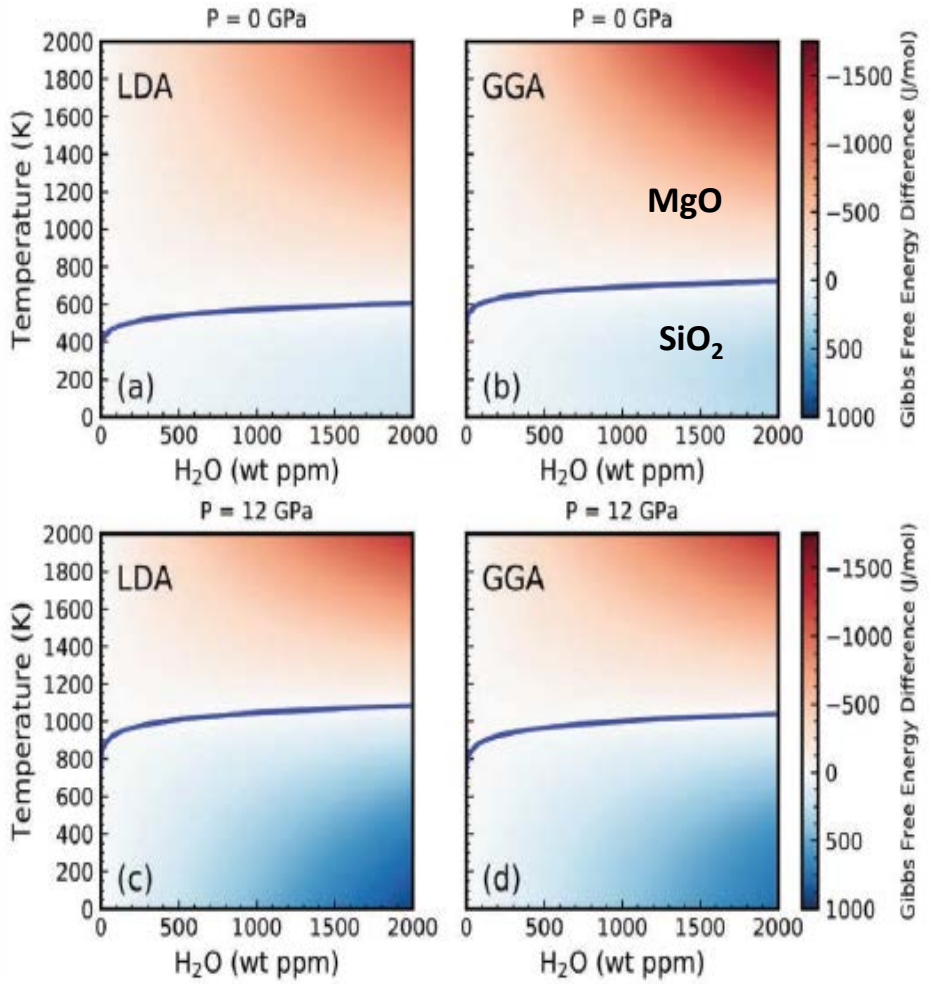

Software for calculation of relevant properties

Computer Physics Communications 243 (2019) 110–120

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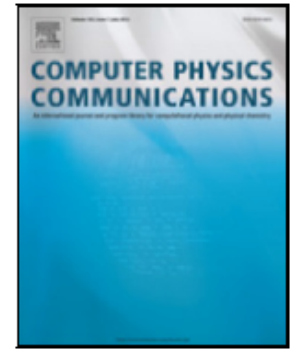
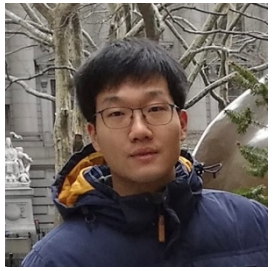


phq: A Fortran code to compute phonon quasiparticle properties and dispersions☆



Z. Zhang [a], D.-B. Zhang [b,c,*], T. Sun [d], R.M. Wentzcovitch [a,e,**]

[a] Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY 10027, USA
[b] College of Nuclear Science and Technology, Beijing Normal University, Beijing 100875, China
[c] Beijing Computational Science Research Center, Beijing 100193, China
[d] Key Laboratory of Computational Geodynamics, Chinese Academy of Sciences, Beijing 100049, China
[e] Department of Earth and Environmental Sciences, Lamont-Doherty Earth Observatory, Columbia University, New York, NY 10964, USA

Note: “Phonopy” – Quasiparticle properties only. No phonon dispersion.

Software for calculation of relevant properties

Phonon Quasiparticle Approach

Step 1 – Mode-projected Velocity Auto-correlation Function

Using MD and $\hat{\boldsymbol{e}}_{\boldsymbol{qs}}$ from harmonic phonon calculation:

$$\langle V_{\mathbf{q}s}(0) \cdot V_{\mathbf{q}s}(t) \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} V_{\mathbf{q}s}^*(t') V_{\mathbf{q}s}(t'+t) dt'$$

where,

$$V_{\mathbf{q}s}(t) = \sum_{i=1}^{N} V(t) \cdot e^{i\mathbf{q}\cdot\mathbf{r}_i} \cdot \hat{\mathbf{e}}_{\mathbf{q}s}.$$

$$V(t) = V\left(\sqrt{M_1}\mathbf{v}_1(\mathrm{t}), \ldots, \sqrt{M_N}\mathbf{v}_N(\mathrm{t})\right)$$

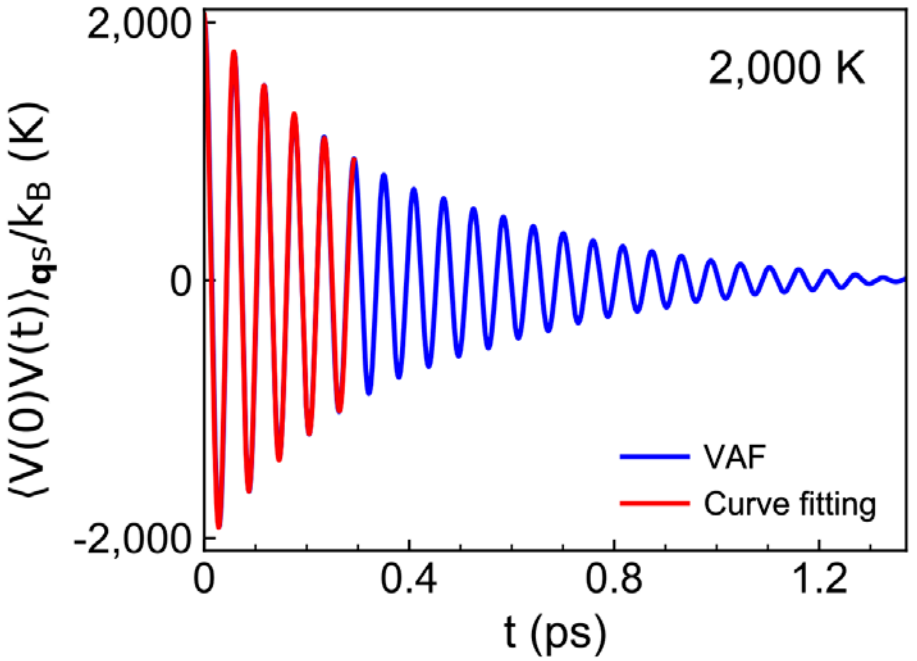
Step 2- phenomenologic fitting the VAF to:

$$\langle V_{\mathbf{q}s}(0) \cdot V_{\mathbf{q}s}(t) \rangle = A_{\mathbf{q}s} \cos(\tilde{\omega}_{\mathbf{q}s} \boldsymbol{t}) e^{-\frac{t}{2\tau_{\mathbf{q}s}}}$$

where: $\tilde{\omega}_{\mathbf{q}s}$ is the renormalized frequency, and

$\tau_{\mathbf{q}s}$ is the phonon lifetime.

VAF and curve fitting:

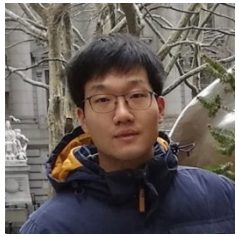


cubic $CaSiO_3$-Pv

Sun and Allen, PRB (2010)
Zhang, Sun, Wetnzcovitch, PRL (2014)

Software for calculation of relevant properties

Phonon Quasiparticle Approach



Step 3 – Phonon dispersion

$$\widetilde{D}(\mathbf{q}) = [\hat{\mathbf{e}}_{\mathbf{q}}]\Omega_{\mathbf{q}}[\hat{\mathbf{e}}_{\mathbf{q}}]^{\dagger}$$

where,

$\Omega_{\mathbf{q}} = \mathrm{diag}[\widetilde{\omega}^2_{\mathbf{q}1}, \widetilde{\omega}^2_{\mathbf{q}2}, \dots, \widetilde{\omega}^2_{\mathbf{q}3N}]$, and

$\hat{\mathbf{e}}_{\mathbf{q}} = [\hat{\mathbf{e}}_{\mathbf{q}1}, \hat{\mathbf{e}}_{\mathbf{q}2}, \dots, \hat{\mathbf{e}}_{\mathbf{q}3N}]$.

Effective harmonic force constant matrix:

$\widetilde{\Phi}(\mathbf{r}) = \sum_{\mathbf{q}} \widetilde{D}(\mathbf{q}) \cdot e^{i\mathbf{q}\cdot\mathbf{r}}$, and

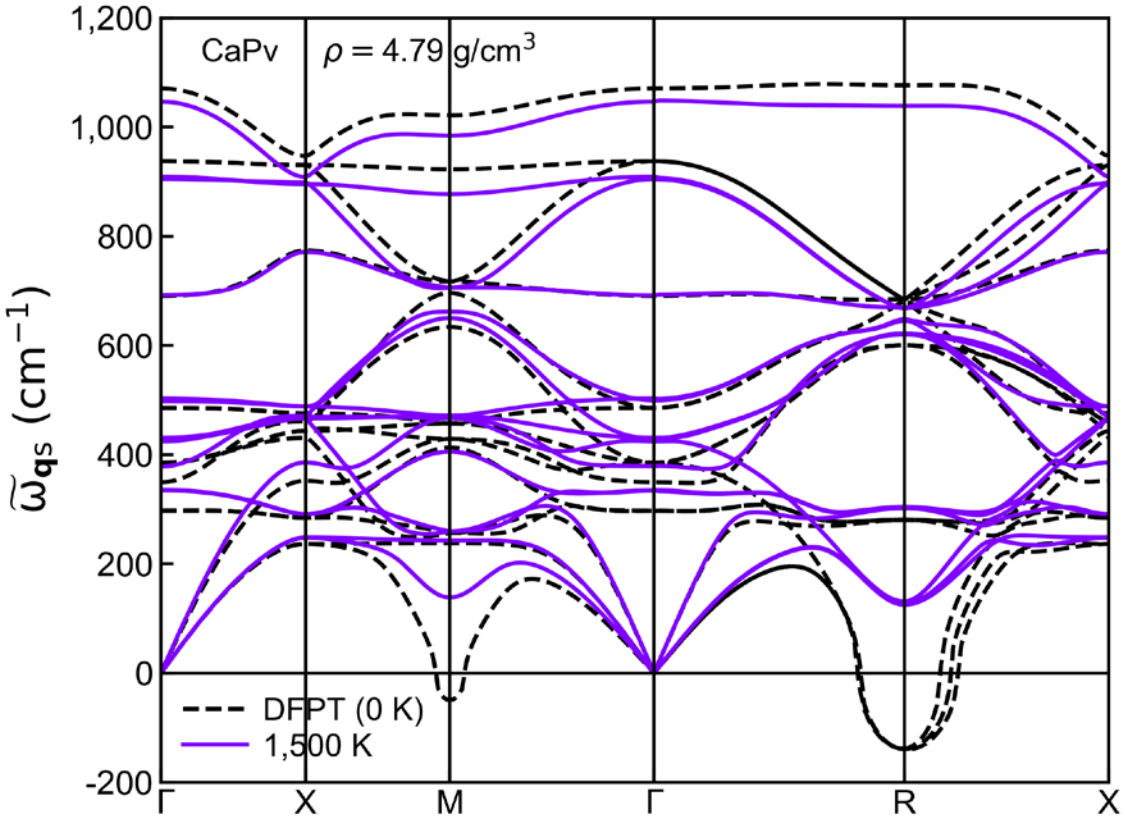
effective harmonic dynamical matrix at any $\mathbf{q}'$:

$\widetilde{D}(\mathbf{q}') = \sum_{\mathbf{r}} \widetilde{\Phi}(\mathbf{r}) \cdot e^{-i\mathbf{q}'\cdot\mathbf{r}}$.

By diagonalizing $\widetilde{D}(\mathbf{q}')$, we can obtain the renormalized phonon dispersion. (Fourier interpolation)

Renormalized phonon dispersion:

cubic $CaSiO_3$-Pv (T > 700 K P > 22 GPa)



Note: “Phonopy” – Quasiparticle properties only. No phonon dispersion.

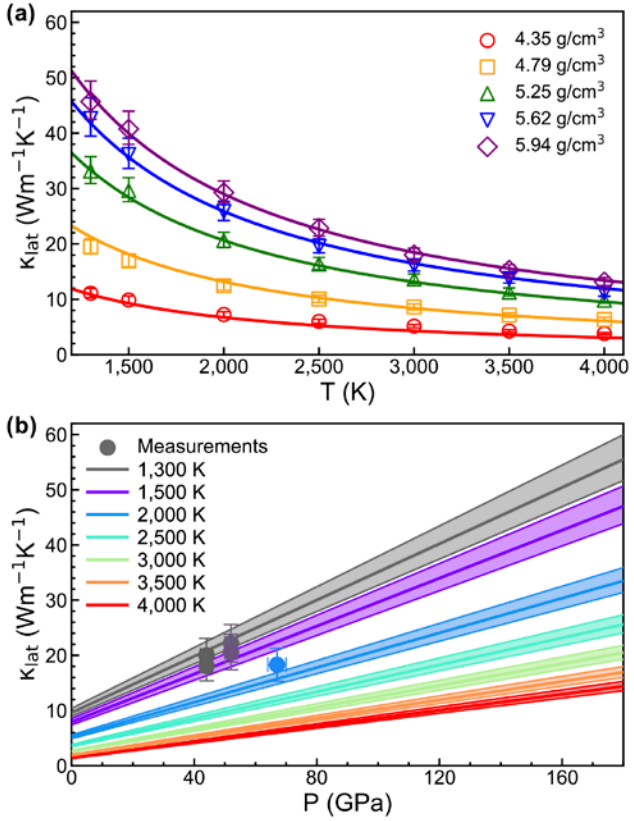
Software for calculation of relevant properties

Lattice thermal conductivity of cubic CaPv

Boltzmann transport equation: $c_{\mathbf{q}s}$, $v_{\mathbf{q}s}$, and $\tau_{\mathbf{q}s}$ are mode heat capacity, group velocity, and lifetime, respectively.

$$\kappa = \frac{1}{3}\sum_{\mathbf{q}s} c_{\mathbf{q}s} v_{\mathbf{q}s}^2 \tau_{\mathbf{q}s}$$

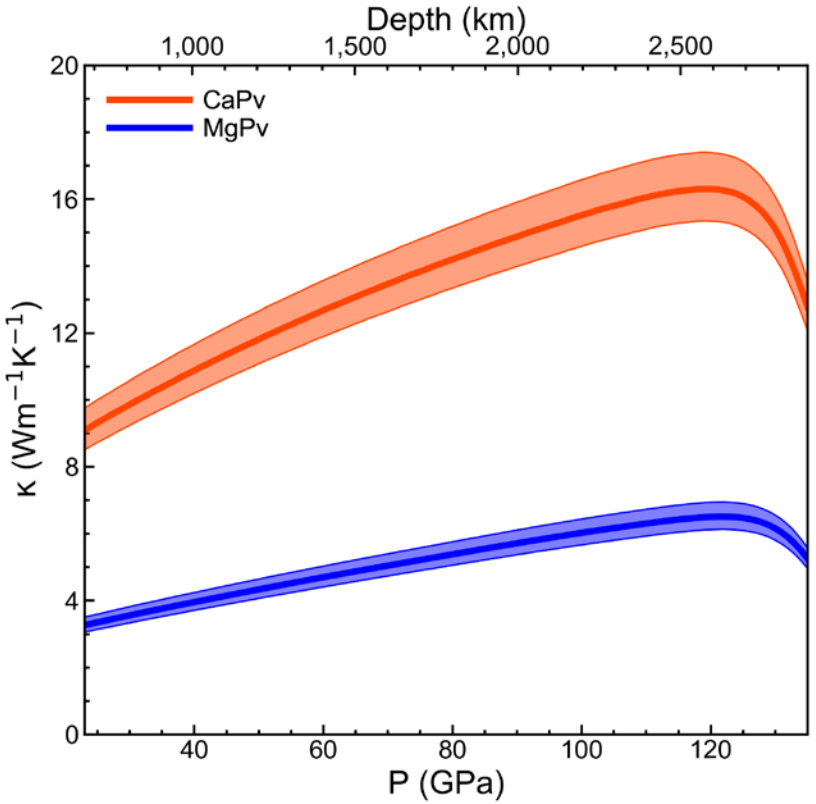
***T*- and *P*-dependence of κ(CaPv):**



$\frac{1}{T^{1.11}}$ dependence on *T*

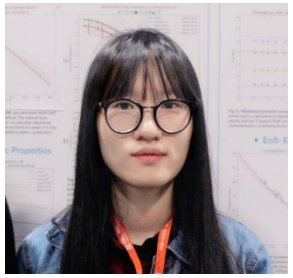
Linear dependence on *P*

κ(CaPv) along the geotherm:



Zhang, Wentzcovitch, Zhang, Ohta, Hirose, *Phys. Rev. Lett.*, under review (2021)

Software for calculation of relevant properties



PGM: A Python code for anharmonic thermodynamics

J. Zhuang, H. Wang, Q. Zhang, and R. Wentzcovitch, *Comp. Phys. Comm. (in prep.)*

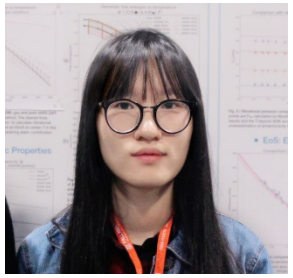
"Harmonic" insulators (QHA) (N→ ∞)

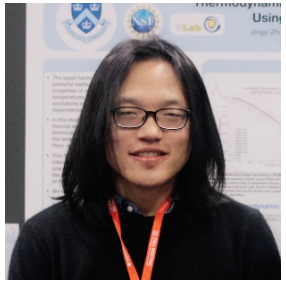
$$F(T,V) = F_{st}(V) + F_{vib}(T,V)$$

$$F_{vib}(T,V) = \frac{1}{2}\sum_{\boldsymbol{q},s} \hbar\omega_{\boldsymbol{q},s}(V) + k_B T \sum_{\boldsymbol{q},s} \ln\left(1 - \exp\left(-\frac{\hbar\omega_{\boldsymbol{q},s}(V)}{k_B T}\right)\right),$$

$$n_{\boldsymbol{q}s}(T,V) = \frac{1}{\exp\frac{\hbar\omega_{\boldsymbol{q}s}(V)}{k_B T} - 1}$$

Software for calculation of relevant properties





PGM: A Python code for anharmonic thermodynamics

J. Zhuang, H. Wang, Q. Zhang, and R. Wentzcovitch, *Comp. Phys. Comm. (in prep.)*

"Anharmonic" metals (N→ ∞)

Calculations done with the **Mermin** functional

$$F(T_{el}, T_{ion}, V) = F_{st}(T_{el}, V) + F_{vib}(T_{el}, T_{ion}, V)$$

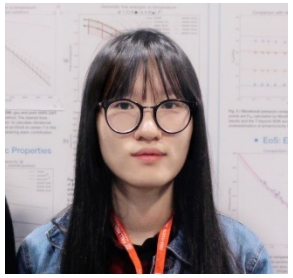
$$S_{vib}(T_{el}, T_{ion}, V) = k_B \sum_{\boldsymbol{q},s} \Big((1 + n_{\boldsymbol{q}s}) \ln(1 + n_{\boldsymbol{q}s}) - n_{\boldsymbol{q}s} \ln n_{\boldsymbol{q}s} \Big)$$

$$n_{\mathbf{qs}}(T_{ion}, T_{el}, V) = \frac{1}{\exp \frac{\hbar \tilde{\omega}_{\mathbf{qs}}(T_{ion}, T_{el}, V)}{k_B T_{ion}} - 1}$$

$$F_{vib}(T_{el}, T_{ion}, V) = F_{zp}(T_{el} = 0, T_{ion} = 0, V) - \int_0^{T_{ion}} S_{vib}(T_{el} = T', T_{ion} = T', V) dT'$$

$$S_{tot}(T_{el}, T_{ion}, V) = S_{el}(T_{el}, V) + S_{vib}(T_{el}, T_{ion}, V)$$

Software for calculation of relevant properties



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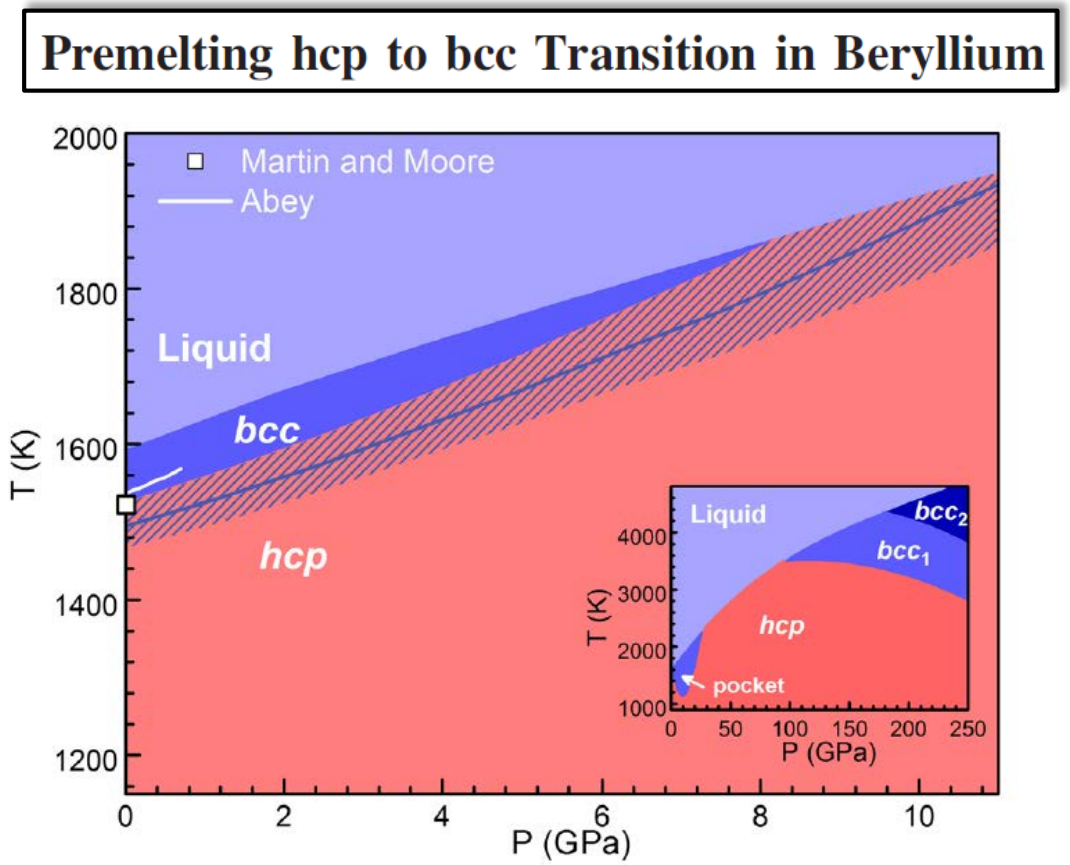
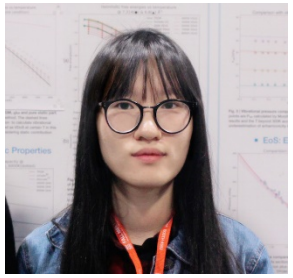


Y. Lu, T. Sun, P. Zhang, D. B. Zhang, and R. M. Wentzcovitch, Physical Review Letters **118**, 145702 (2017).

Software for calculation of relevant properties

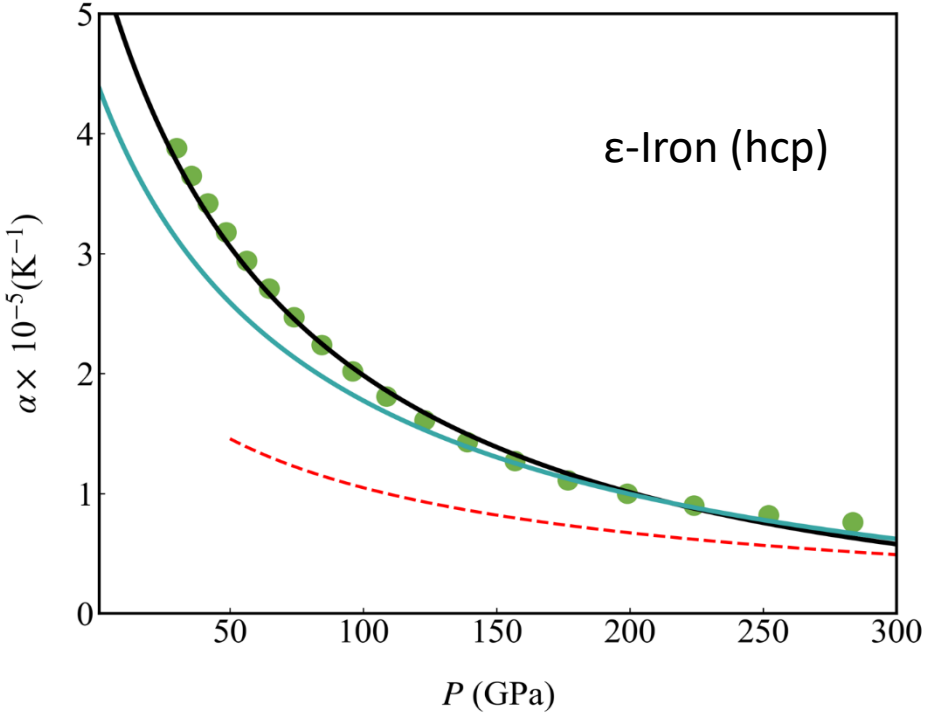


PGM: A Python code for anharmonic thermodynamics

J. Zhuang, H. Wang, Q. Zhang, and R. Wentzcovitch, *Comp. Phys. Comm. (in prep.)*

Thermodynamic properties of ε-Fe with thermal electronic excitation effects on vibrational spectra

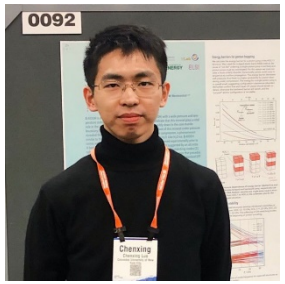
J. Zhuang, H. Wang, Q. Zhang, and R. Wentzcovitch, Phys. Rev. B, in prep. (2020)



- Exp. at 300 K (Anderson *et al.*, 2001)
- PGM
- QHA with T_{el} = 300 K (Mermin)
- $F_{st}(T_{el},V) + F_{vib}(300\ K, V)$

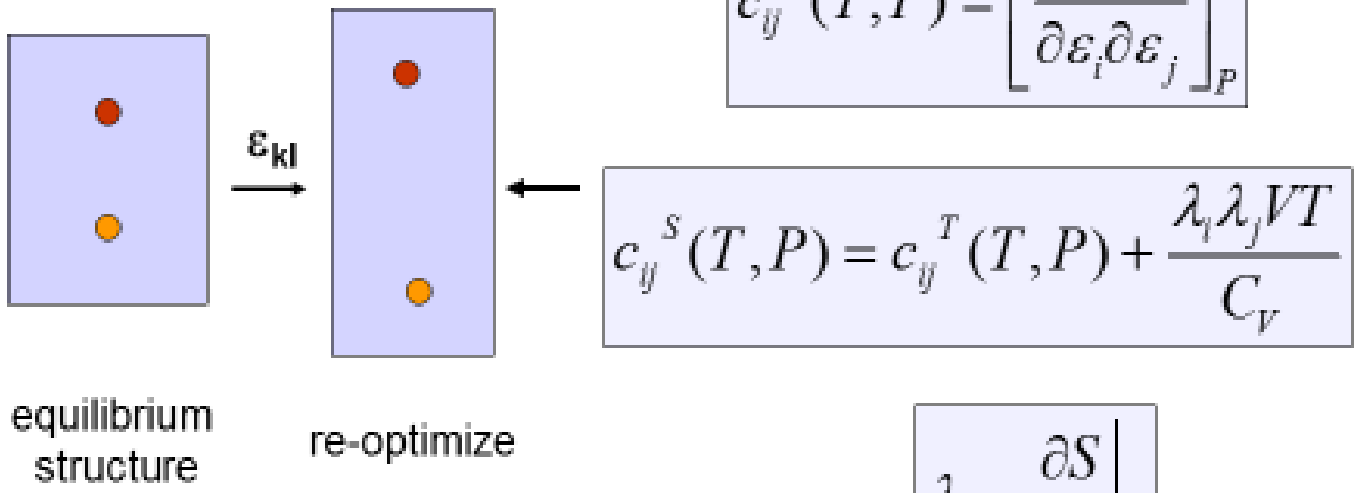
Note: "Phonopy" – Includes electronic excitation effects on $F_{st}(T_{el})$, not anharmonicity.

Software for calculation of relevant properties



SAM-Cij: A Python code for thermoelasticity

C. Luo, R. Wentzcovitch, Z. Wu, and W. Wang, *Comp. Phys. Comm. (in press)*

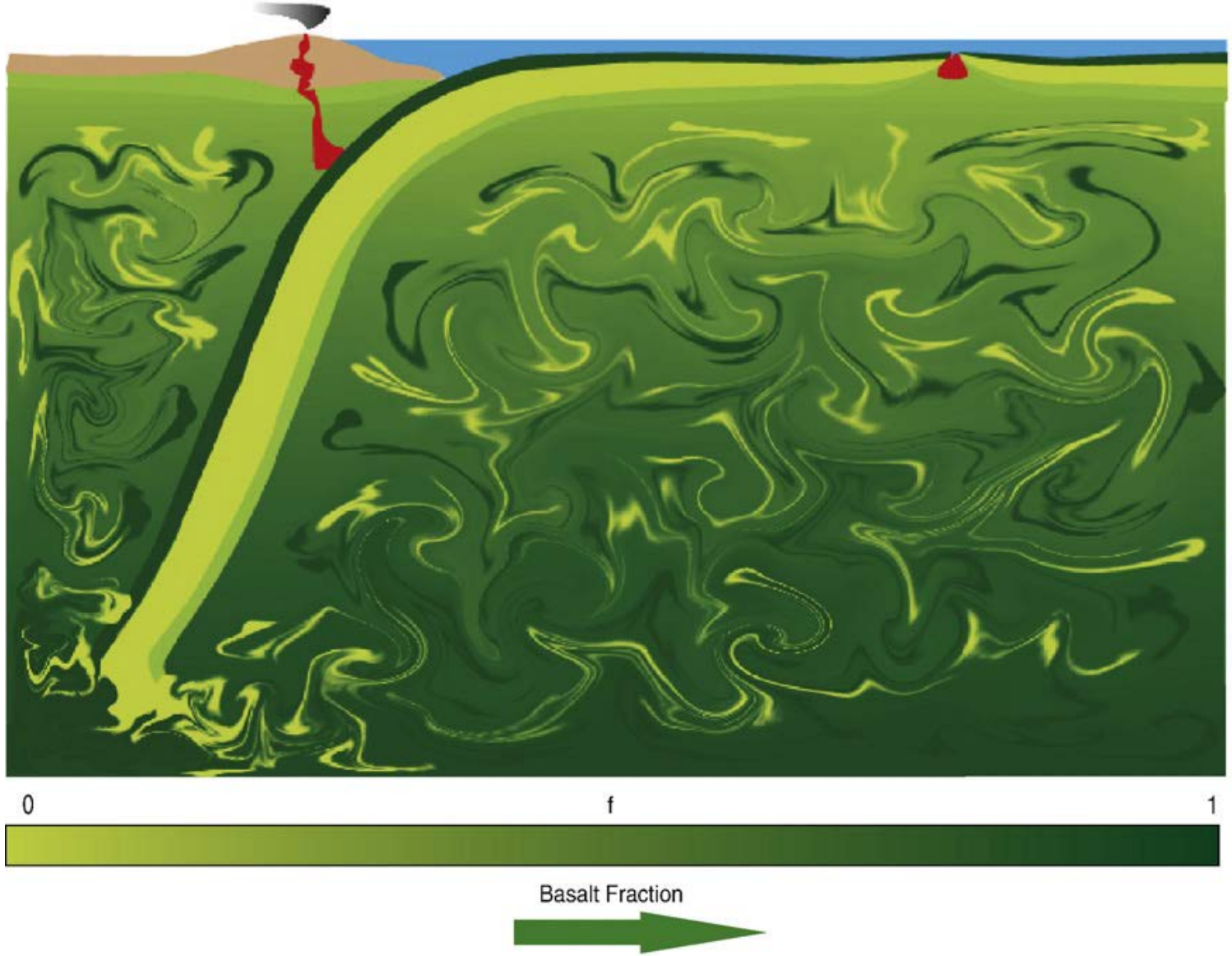


"Method" Karki et al., *Science* (1999), Wentzcovitch et al., *PRL* (2004) – Fully numerical

Wu and Wentzcovitch, *PRB* (2011) – Semi-analytical method (SAM)

Wu, Wang, Wentzcovitch, *PRB* (2019) – SAM extended to all symmetries

Lower mantle small scale heterogeneities



Basaltic crust (MORB)

Harzburgite

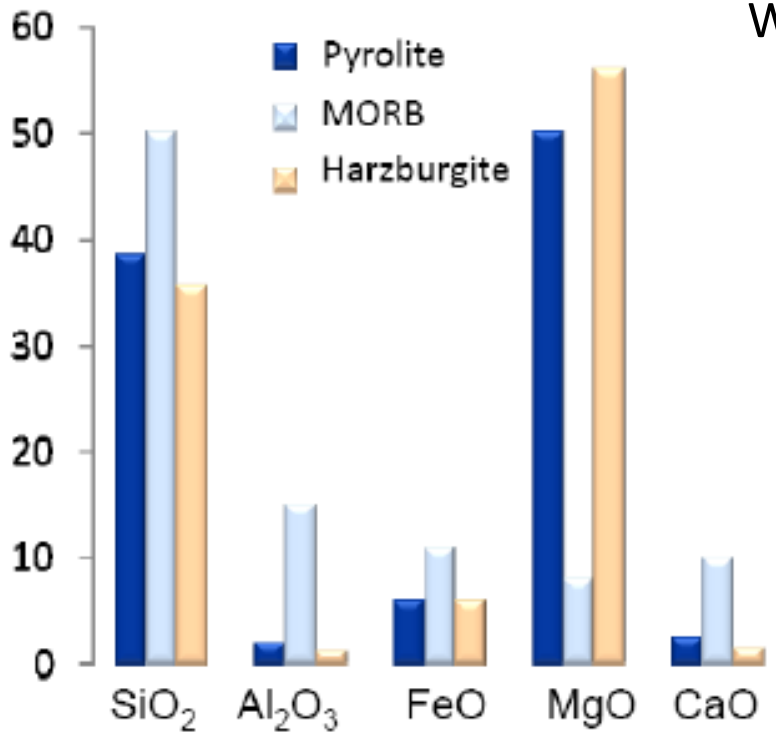
Peridotite

+ 3 = Pyrolite

Common small scale (~10 Km) low V_s heterogeneities (up to -10%) between 1400-1700 km depth

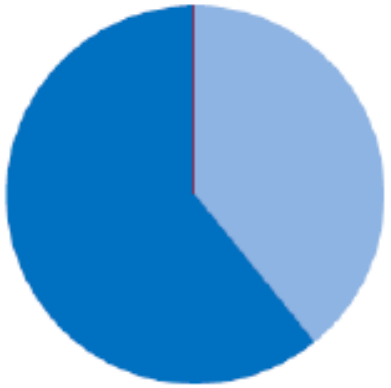
Lower mantle heterogeneities

What is the seismic signature of MORB crust in a pyrolytic mantle??

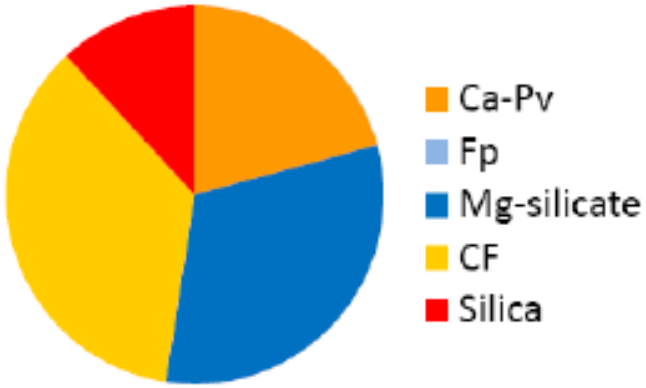


a) Bulk composition

b) Pyrolite



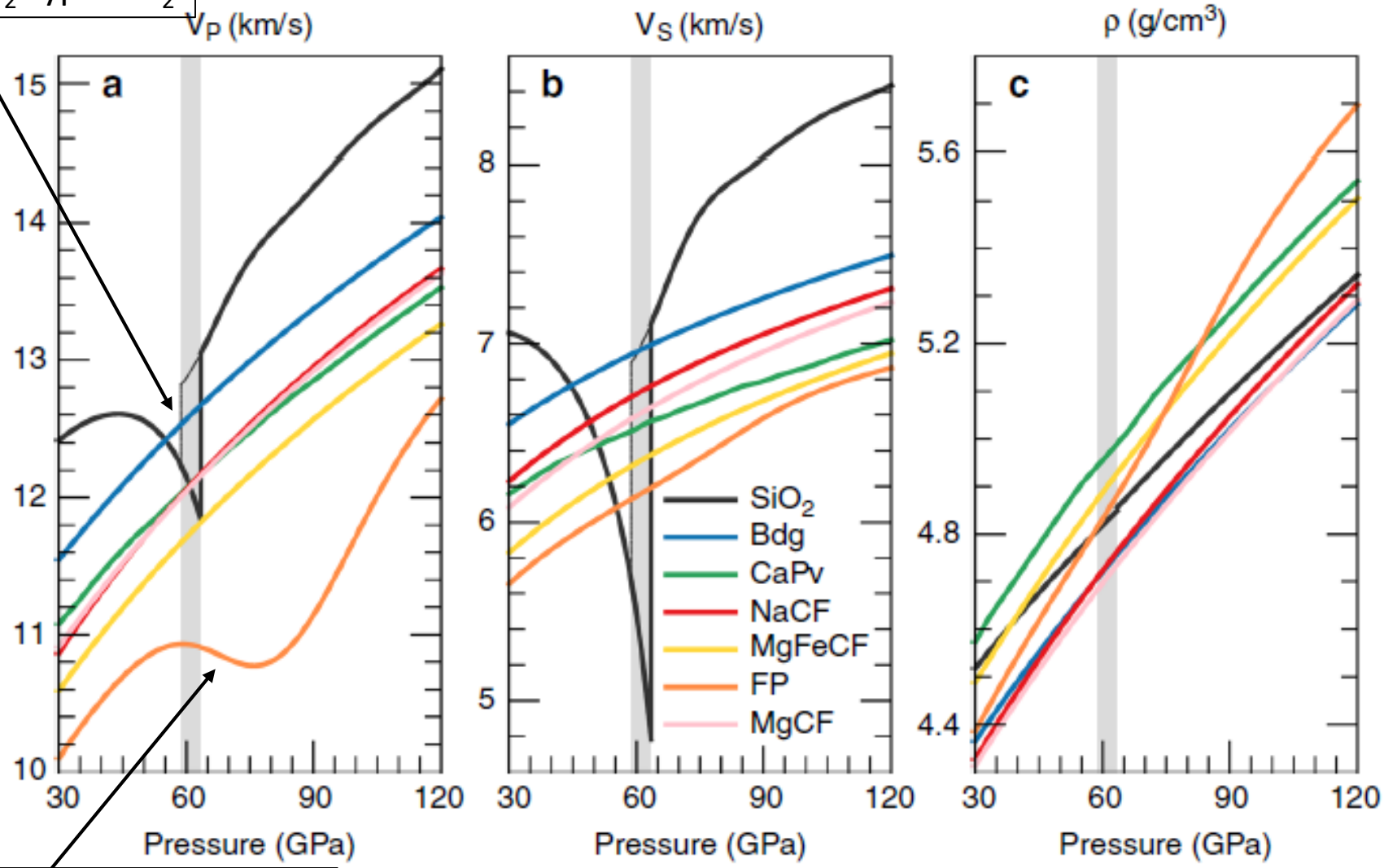
c) Harzburgite



d) MORB

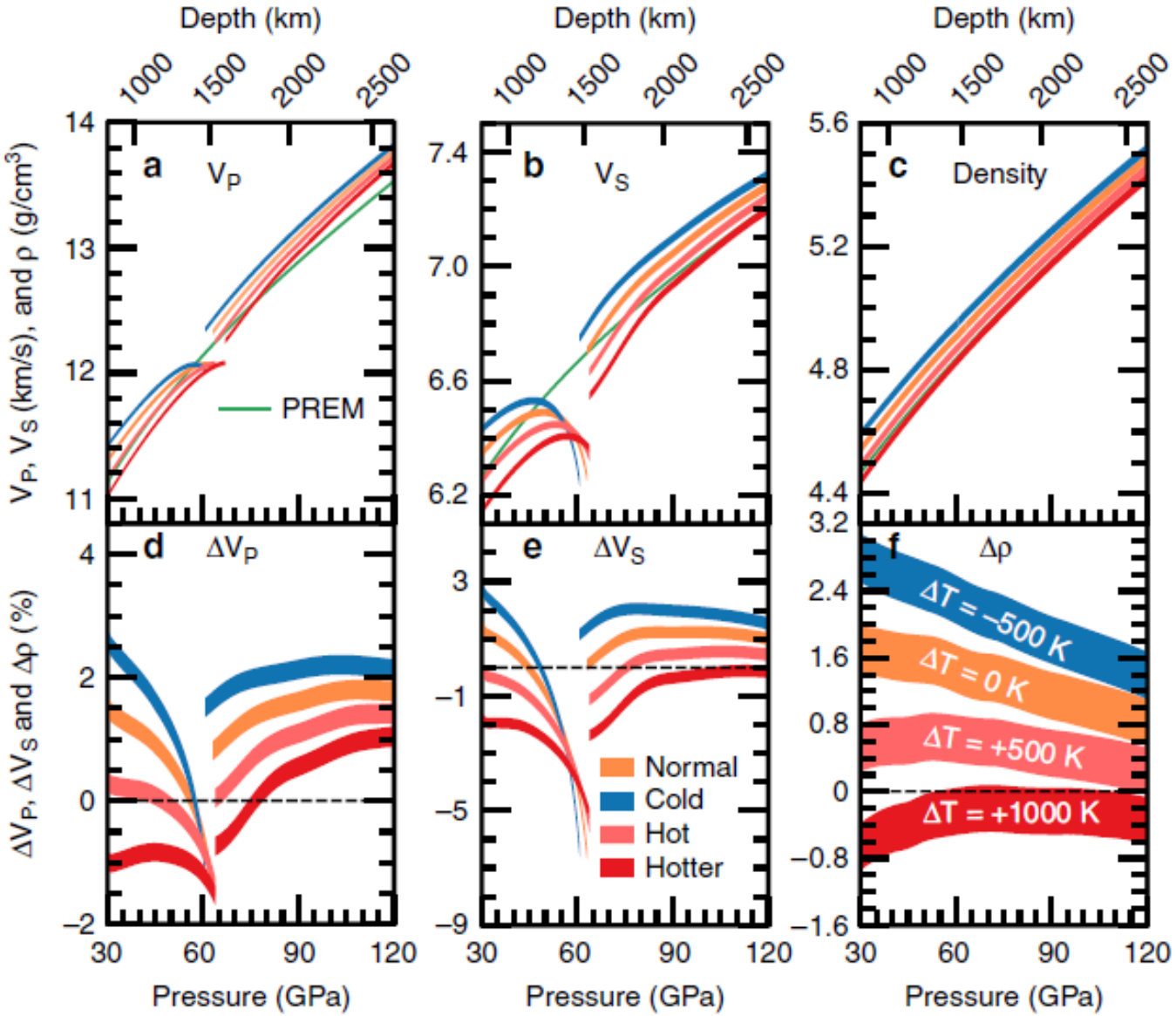
Lower mantle heterogeneities

stishovite → $CaCl_2$-type SiO_2

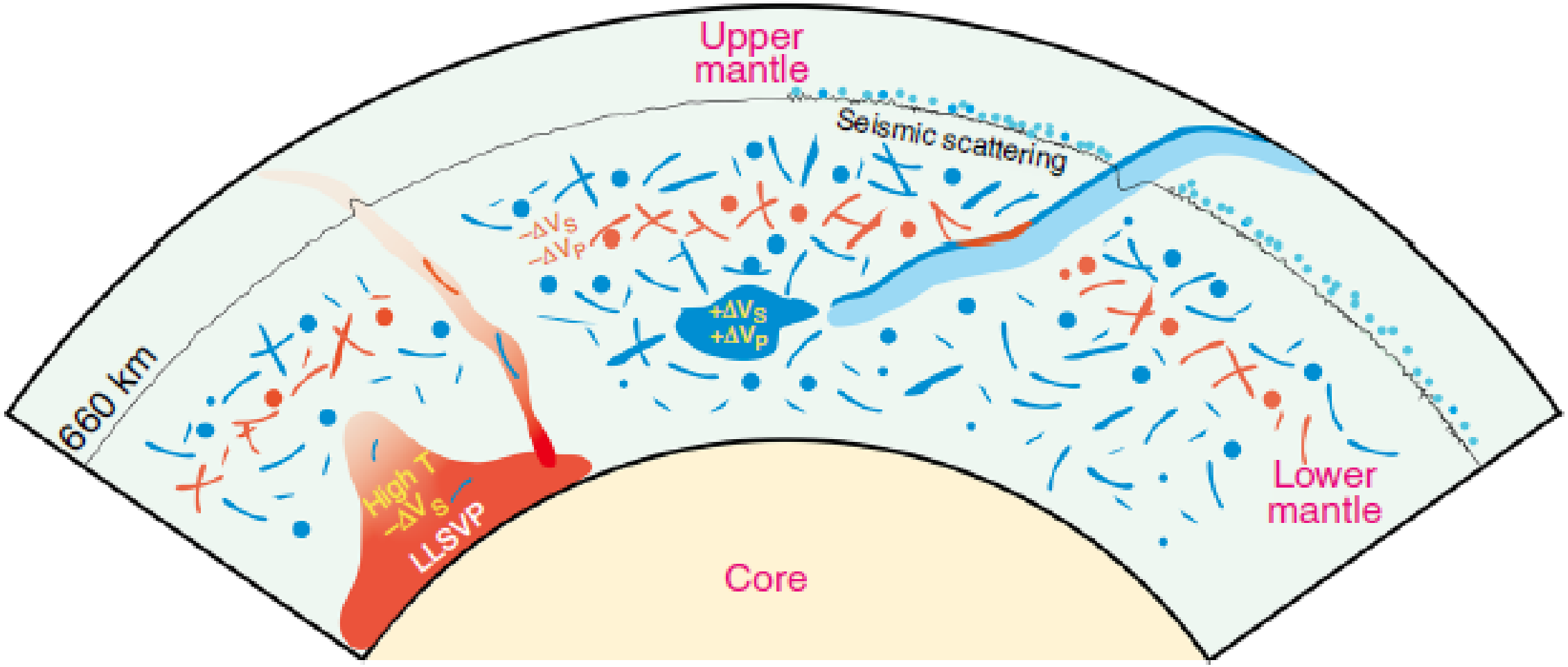


Spin transition in Fe in $Mg_{(1-x)}Fe_xO$

Lower mantle heterogeneities



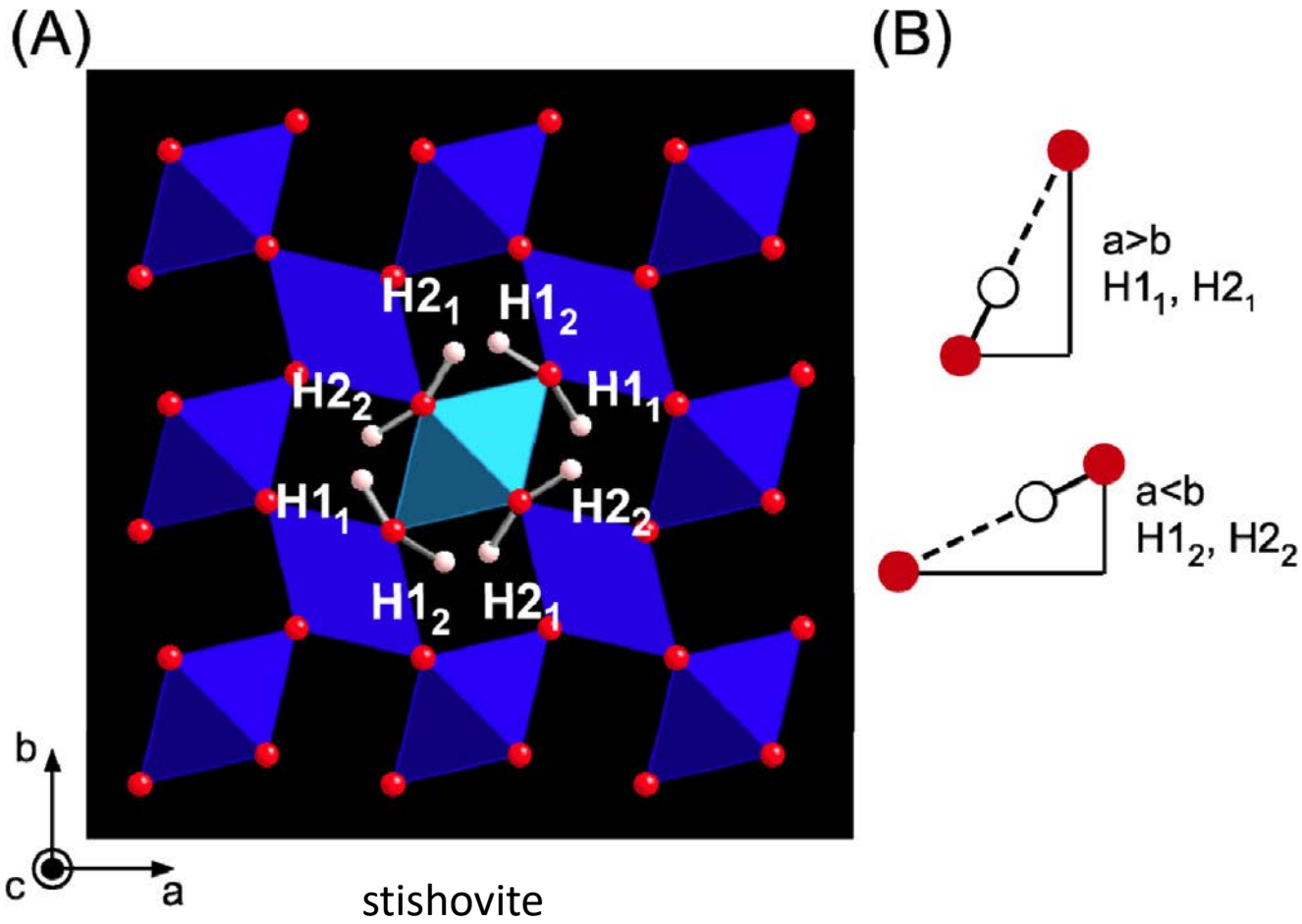
Signature of MORB crust in a pyrolytic mantle



W. Wang, Y. Xu, D. Sun, S. Ni, R. Wentzcovitch, Z. Wu, *Nat. Comm*. (2020), DOI: 10.1038/s41467-019-13720-2

Post-stishovite transition in hydrous aluminous SiO_2

Experiments: 2 mol% AlOOH reduces the stishovite → $CaCl_2$-type SiO_2 by 25 GPa (50%)



stishovite

Physics of the Earth and Planetary Interiors 255 (2016) 18–26

Contents lists available at ScienceDirect

Physics of the Earth and Planetary Interiors

journal homepage: www.elsevier.com/locate/pepi

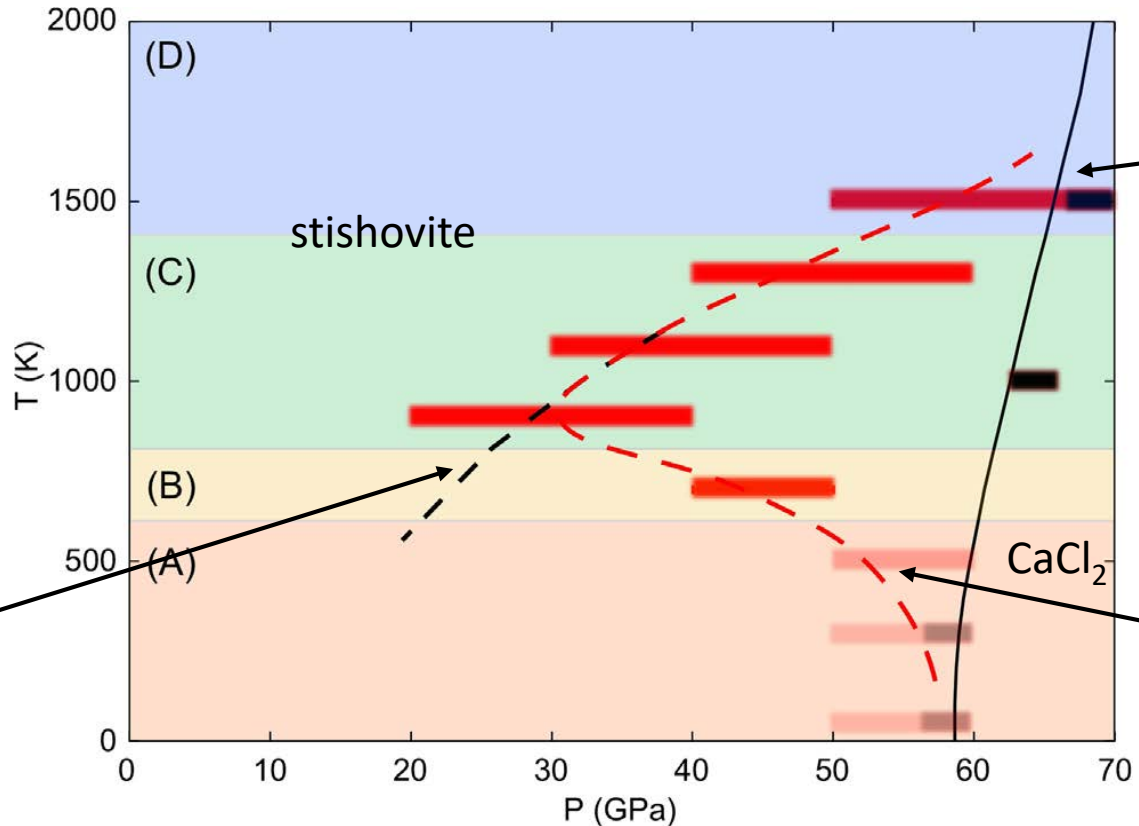
Post-stishovite transition in hydrous aluminous SiO_2

Koichiro Umemoto [a,b,*], Katsuyuki Kawamura [c], Kei Hirose [b,d,e], Renata M. Wentzcovitch [b,f,g]

MD on ~4700 atoms (IP)

8x8x12 supercell (96 H)

6.25 mol% of AlOOH in SiO_2



Super-ionic “H”

~Thermodynamic phase boundary

Hysteresis by starting from stishovite with disordered H

Databases and online applications

http://www.mineralscloud.com/resources/

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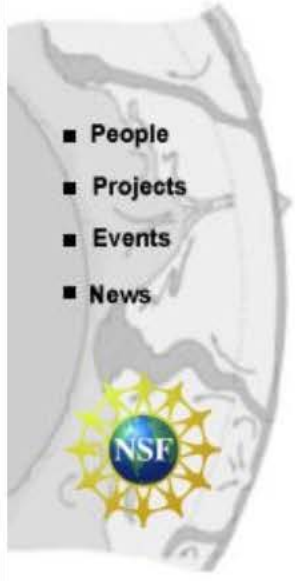
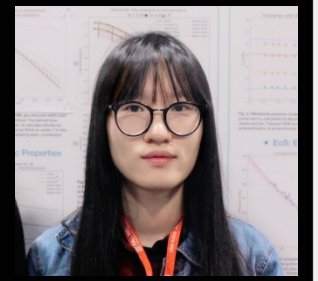
Columbia University

VLab



Resources

- MgO Pressure Scale Calculator
- NaCl Pressure Scale Calculator
- Thermodynamics of Minerals - ThoM
- Thermodynamics of Minerals at Ultra High Pressures - ThoM UHP
- Thermoelastic Properties of Minerals - TheoM
- Rare Earth PAW datasets
- Rock Properties Calculator
- Crystal Structure Input Database
- PAW Datasets Library
- Software



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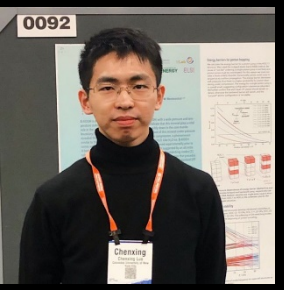
Min. Soc. Am. – crystal structure database (~ 10^3 phases)

Crystal Structure Input Database

The input database below contains the minerals in the Earth's crust and mantle.

Chemistry Search

- **Acmite** $NaFeSi_2O_6$
- **Akimotoite** $MgSiO_3$
- **Al-Perovskite** Al_2O_3
- **Al-Post-Perovskite** Al_2O_3
- **Al-Rh2O3(II)** Al_2O_3



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Rock property calculator

Instructions

This web service calculates elastic and acoustic properties of mineral aggregates (K_S, K_T, G, ρ, v_p, v_s, possion ratio ν) as in Abers and Hackers (2016). The use is intuitive. Several published rock compositions are available from the dropdown menu but they can be edited. Results can be plotted versus pressure or temperature by choosing of ordinate. Results can be viewed or downloaded in table or plot formats.

> Abers, G. A., & Hacker, B. R. (2016). A MATLAB toolbox and Excel workbook for calculating the densities, seismic wave speeds, and major element composition of minerals and rocks at pressure and temperature. Geochemistry, Geophysics, Geosystems, 17(2), 616-624. doi: 10.1002/2015GC006171

Disclaimer: the code might not execute successfully if the pressure and temperature ranges selected for a particular rock / mineral composition are physically invalid.

Rock composition

Published compositions: [ ] clear display / edit

Phase	Name	Amount (vol)	Formulae
	Total	0.00	

Calculation Detail

Ordinate **Range**

( ) *T* from 0 to 500 °C every 100 °C,

(•) *P* from 0 to 160 GPa every 10 GPa

Calculate

VLab

Thermodynamics Properties of Minerals

People
Projects
Events
News

Instructions: The calculations you may perform on minerals listed below accept input by the user through this page ... Read more

- Mg_2SiO_4 forsterite (LDA) paper1 paper2
- Mg_2SiO_4 forsterite (GGA) paper1
- Mg_2SiO_4 wadsleyite (LDA) paper1 paper2
- Mg_2SiO_4 wadsleyite (GGA)
- Mg_2SiO_4 ringwoodite (LDA) paper1 paper2
- Mg_2SiO_4 ringwoodite (GGA) paper1
- MgO FCC (LDA) paper1 paper2 paper3
- MgO FCC (GGA) paper1
- SiO_2 stishovite (LDA) paper1
- $MgSiO_3$ Pbnm (LDA) paper1 paper2 paper3
- $MgSiO_3$ Pbnm (GGA) paper1
- $MgSiO_3$ high-pressure clinoenstatite C2/c (LDA) paper1
- Al_2O_3 Rh_2O_3(II) paper1
- Al_2O_3 Corundum paper1
- Al_2O_3 Post-Perovskite paper1
- SiO_2 stishovite (LDA) paper1
- SiO_2 stishovite (PBE) paper1
- FeOlivine paper1
- FeRingwoodite paper1

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Temperature Grid for Calculations Mg_2SiO_4 wadsleyite (LDA)

Fill default values

Initial T (K)	Final T (K)	Delta T (K)

EOS Type: Finite strain (polynomial) — Order: 0

- [x] Cell Volume
- [x] Thermal Expansion
- [x] Isothermal Bulk Modulus
- [x] Adiabatic Bulk Modulus
- [x] Entropy
- [x] Isocoric Specific Heat
- [x] Isobaric Specific Heat
- [x] Gruneisen Parameter
- [x] Enthalpy
- [x] Specific Heat

Toggle

Grids for Plotting

Ordinate: P — P Grid Type: Regular — T Grid Type: Regular

Output Temperature Grid (K)

Initial T (K)	Num. of Points	Delta T (K)
	0 Update	

Output Pressure Grid (GPa)

Initial P (GPa)	Num. of Points	Delta P (GPa)
	0 Update	

Download Files | Clean Files | View Data | View Plot | Calculate

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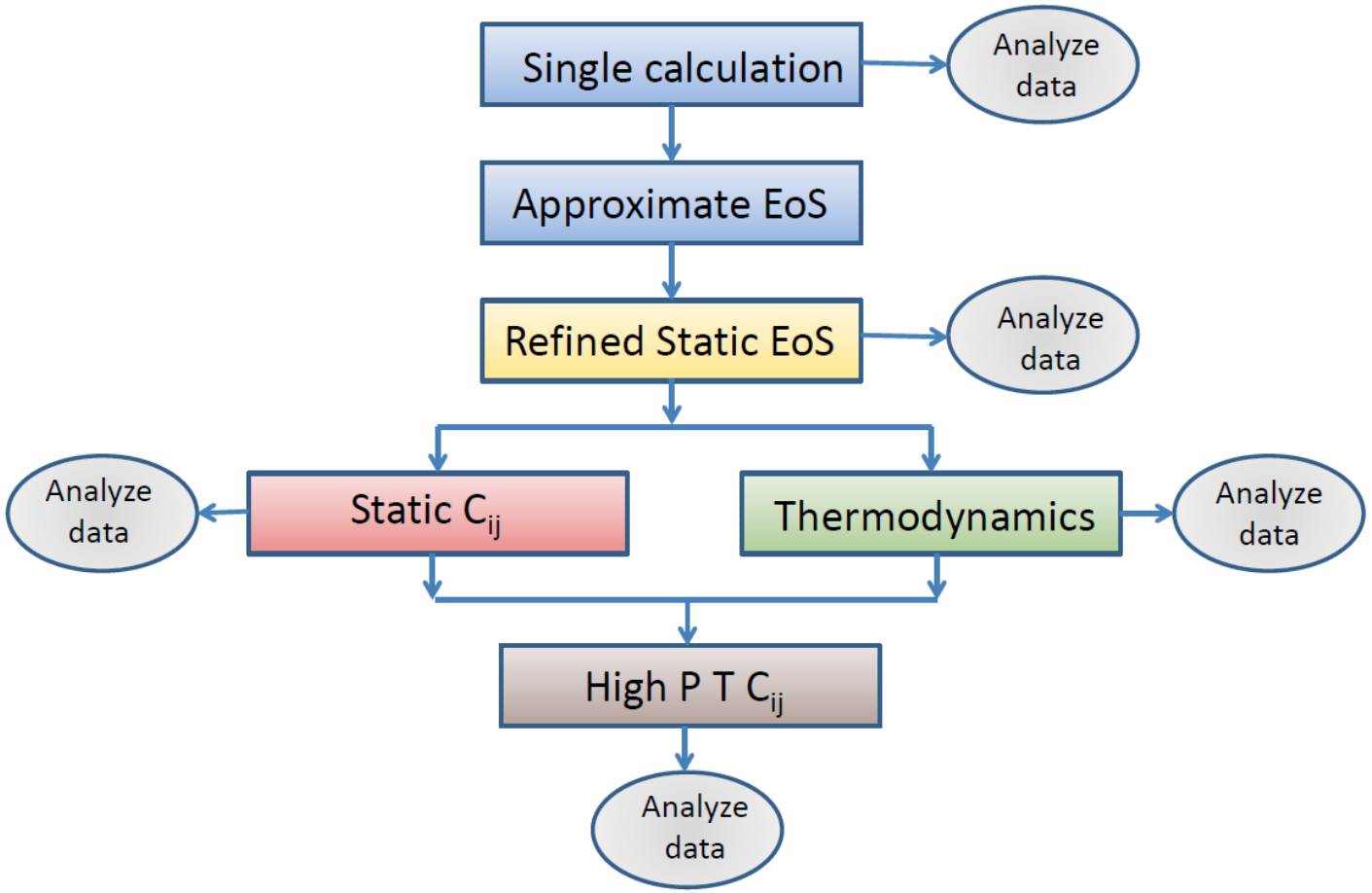
Other research going on:

- EXPRESS workflows in julia



Thank you!