Ab Initio Phase Diagrams of Minerals

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Theoretical Mineral Physics Group at ETH Zurich…

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Plan:

- Introduction
- Simulation Methods
- Results

MgO

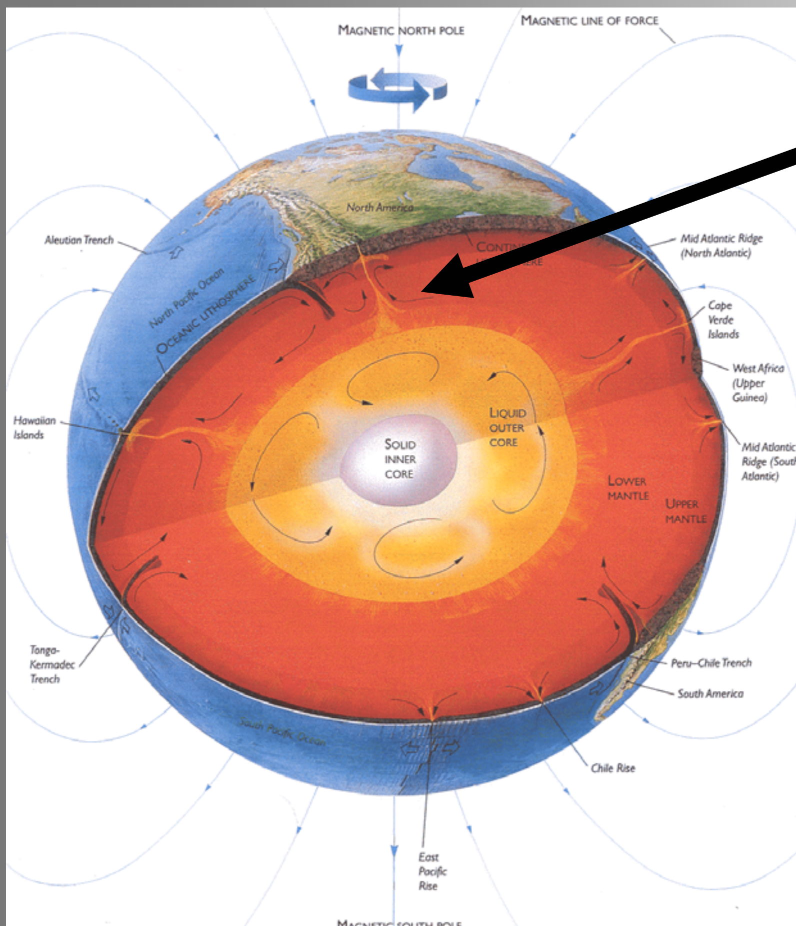
SiO_2

$MgSiO_3$ perovskite and post-perovskite

- Conclusions
- Appendices

1. Introduction

Earth’s Interior

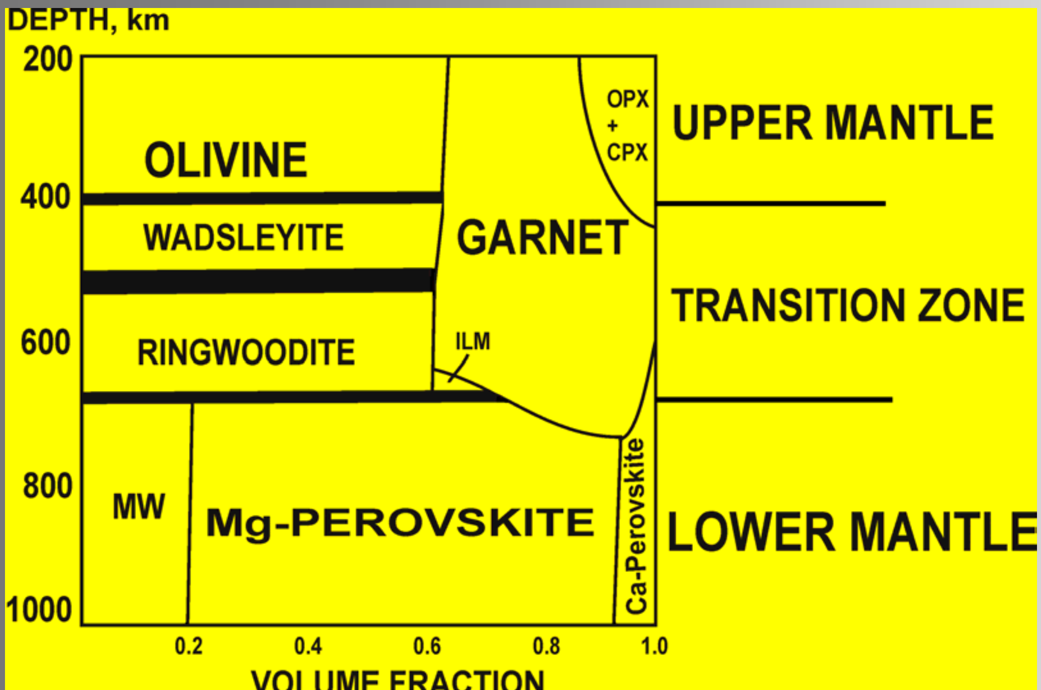


Earth’s structure

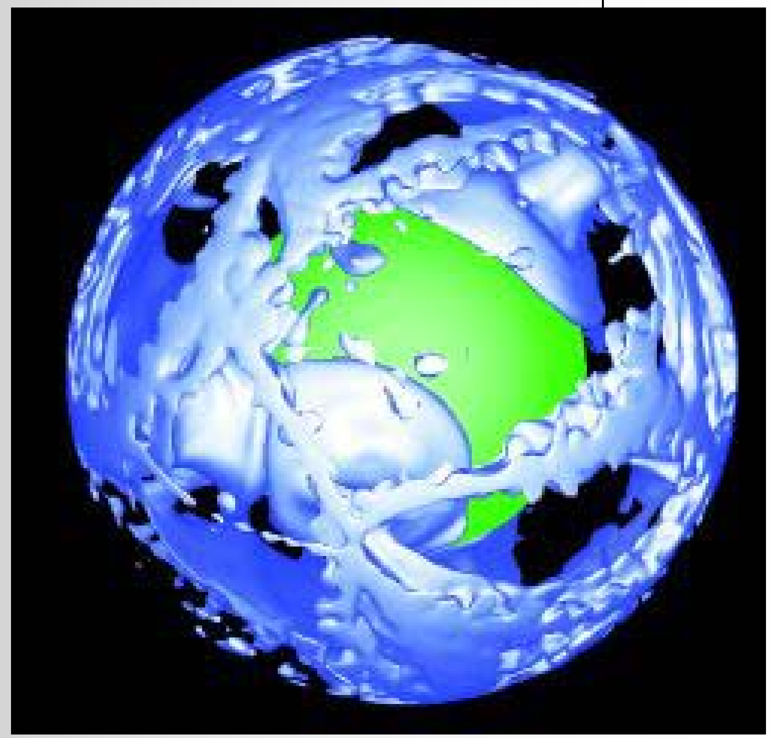
Lower mantle:

- 53 vol.% of the Earth!!!
- 75 vol.% - $MgSiO_3$ perovskite
- 20% - (Mg,Fe)O
- 5% - $CaSiO_3$ perovskite
- Bottom 200 km -**MYSTERY**!!! (D” layer).

Phase Diagrams and Deep Earth



Phase relations in mantle
(after Ringwood, 1991)



Mantle convection: 670 km boundary is a partial barrier
(thanks to P.Tackley)

Seismic discontinuities. Geochemistry. Geodynamics.

Which Diagrams Needed?

- Mantle: MgO-SiO_2-CaO-Al_2O_3-FeO-Fe_2O_3.
- *p,T,x*-phase diagrams, ideally.

Here: pure MgO, SiO_2, $MgSiO_3$.

2. Simulation Methods

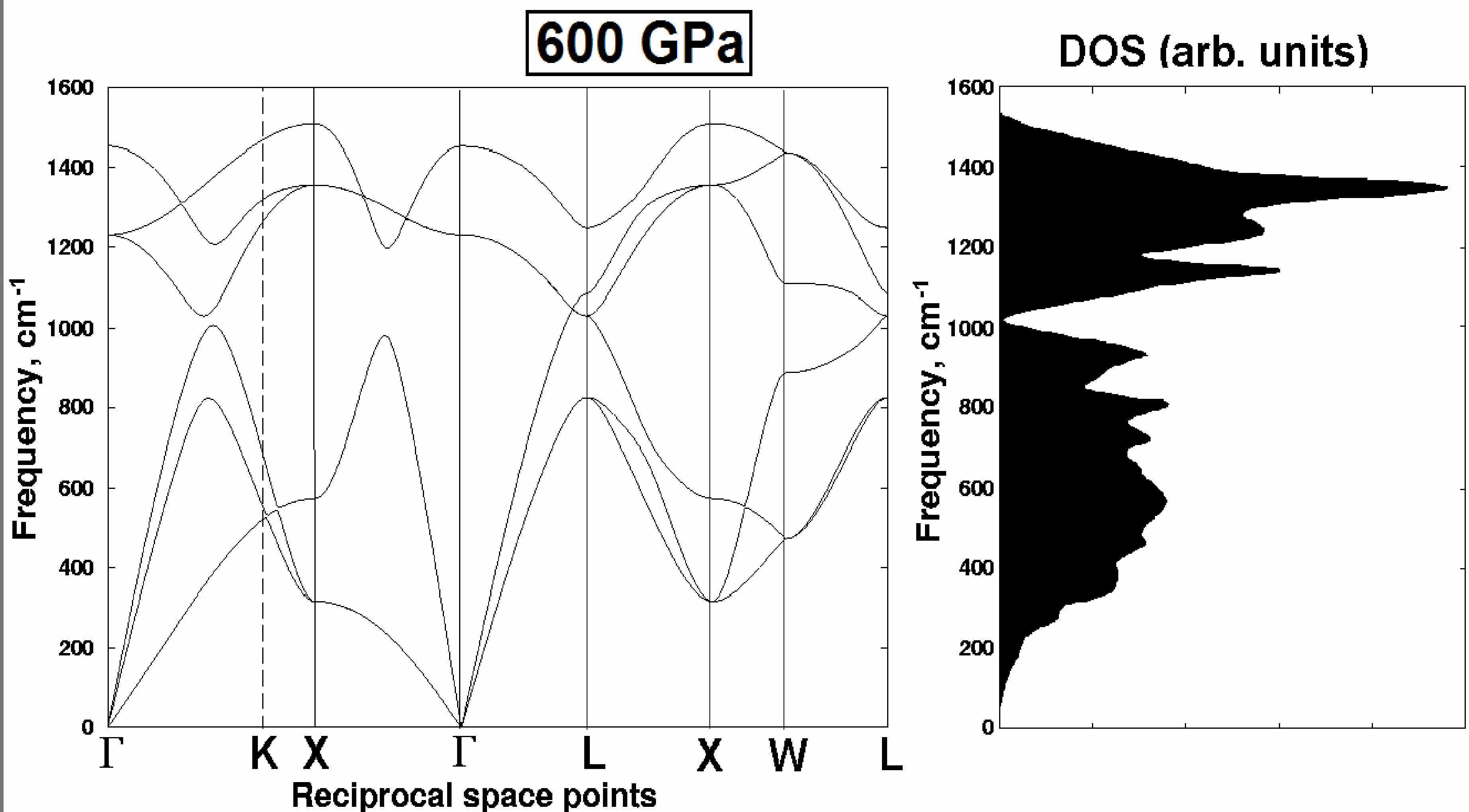
Density-Functional Perturbation Theory

- Quasiharmonic approximation.
- Phonon frequencies $\omega_i(\underline{\mathbf{k}})$ and density of states $g(\omega)$.
- Thermodynamic properties, e.g.:

$$F(T) = E_0 + \int_0^{\omega_{max}} \frac{1}{2}\hbar\omega\, g(\omega)d\omega + k_B T \int_0^{\omega_{max}} \ln[1\text{-}\exp(-\frac{\hbar\omega}{k_B T})]g(\omega)d\omega$$

- G=F+(-dF/dV)V.
- ABINIT code.

Ab Initio Lattice Dynamics

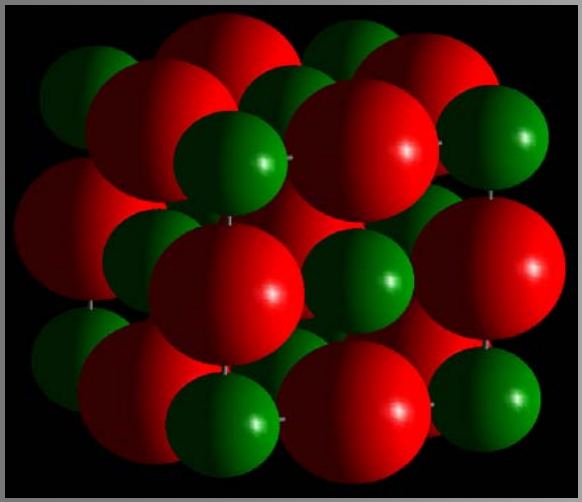


Phonon dispersion curves and phonon density of states of MgO: 0 GPa, 400 GPa, 600 GPa. (Oganov et al., J.Chem.Phys. **118**, 10174 (2003))

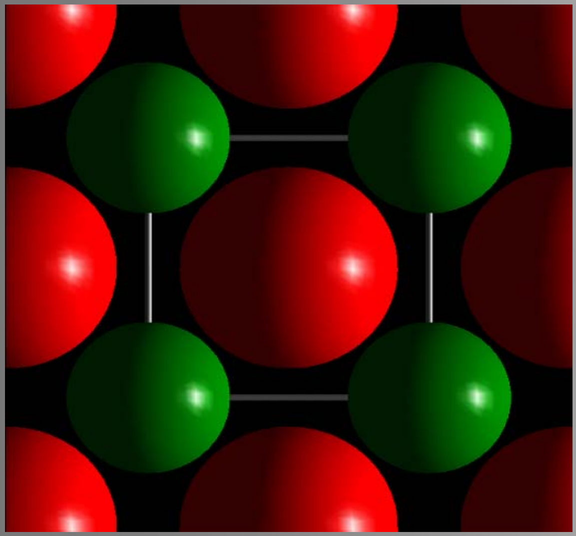
3. Results

Story 1: MgO

B1 vs B2 (not Vitamins!)



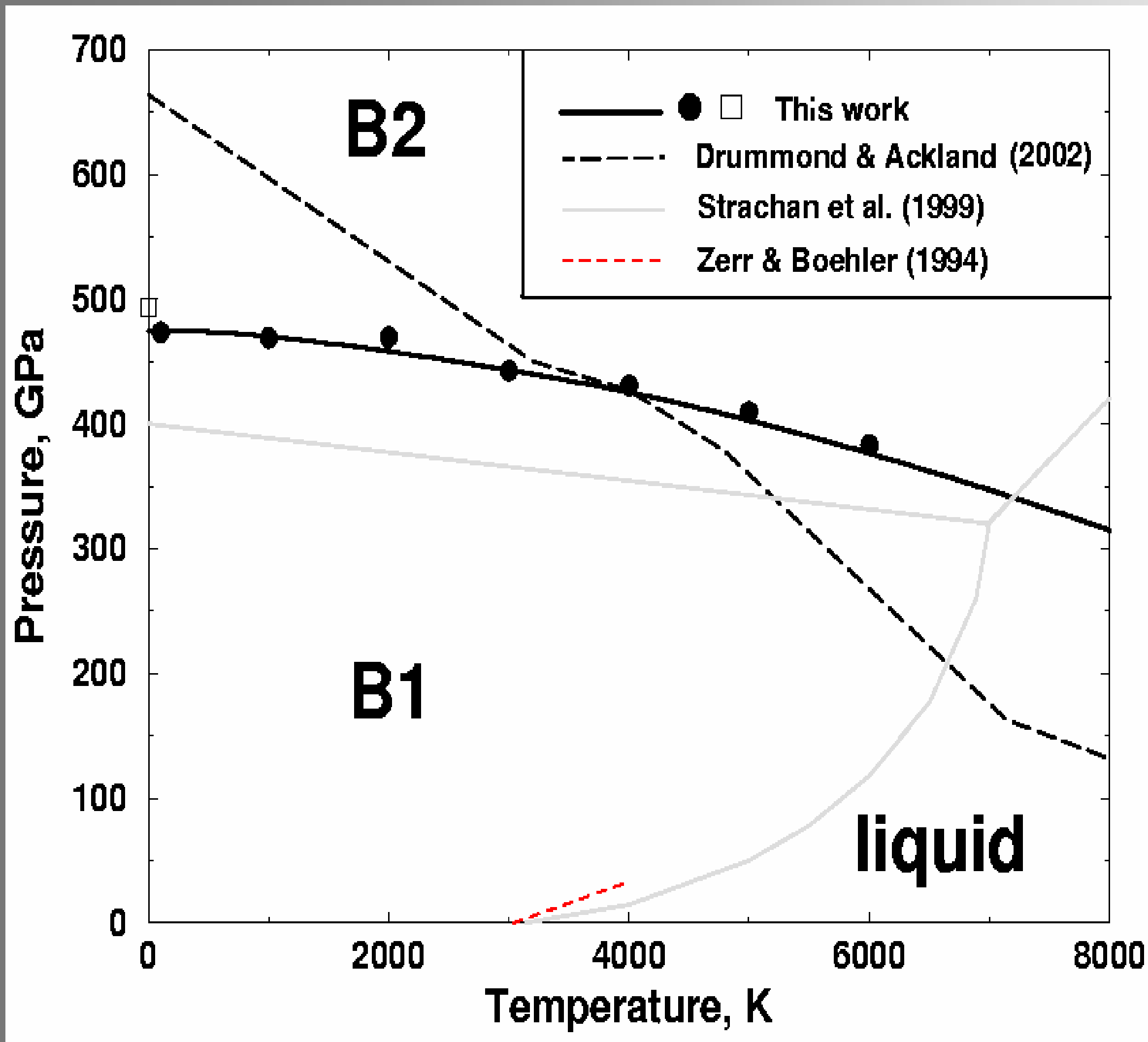
B1



B2

- B1 – structure type NaCl.
- B2 – structure type CsCl.
- Unique stability of the B1 structure!
- Ideal as a pressure calibrant.

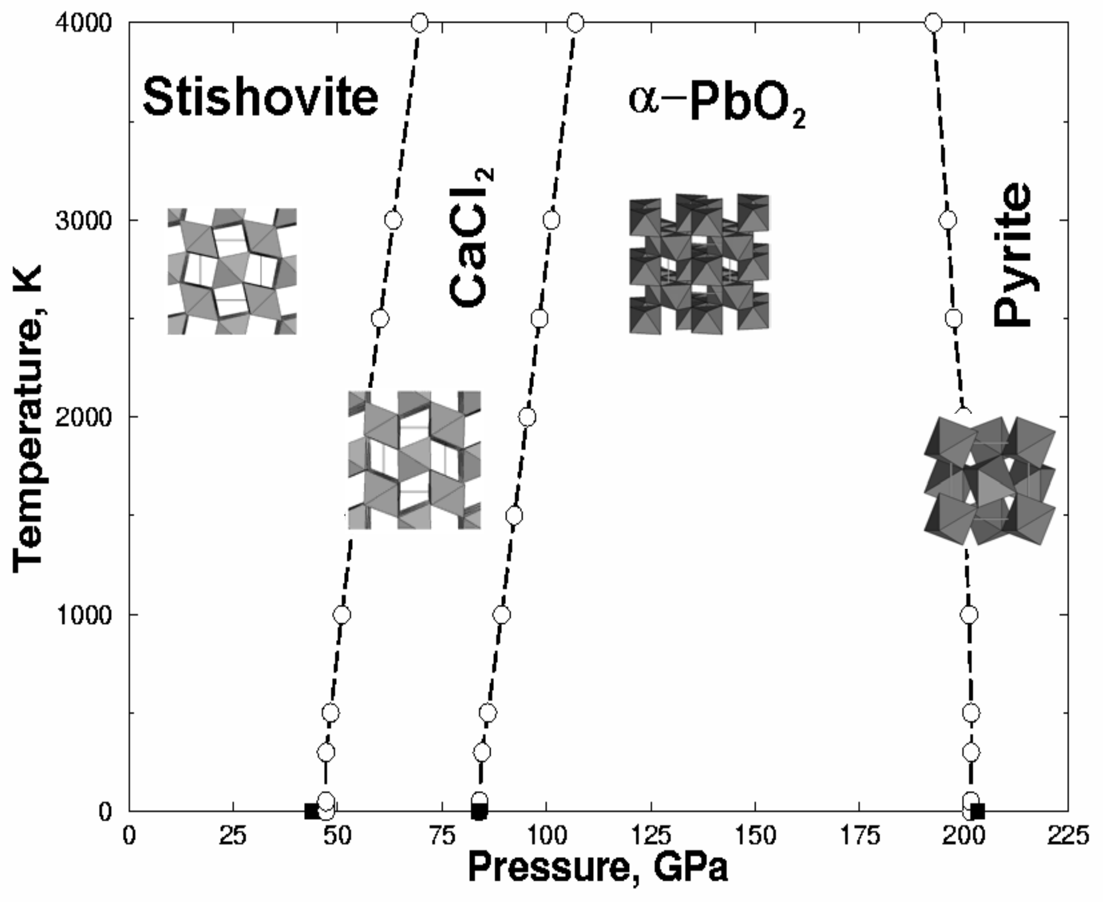
Phase diagram of MgO



Oganov et al., J.Chem.Phys. **118**, 10174 (2003)

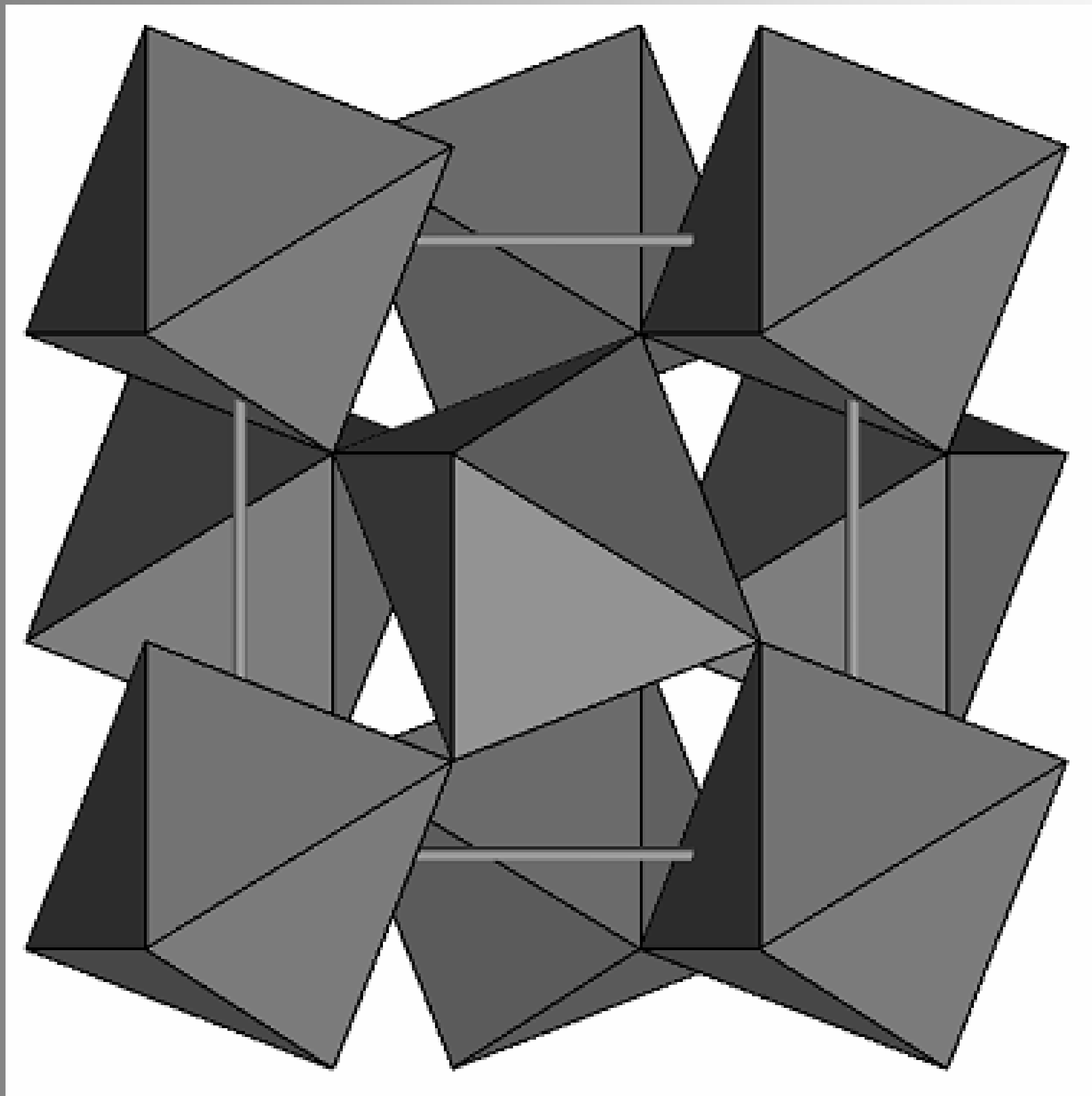
- Only B1 phase in the Earth.

Story 2: Phase diagram of SiO_2



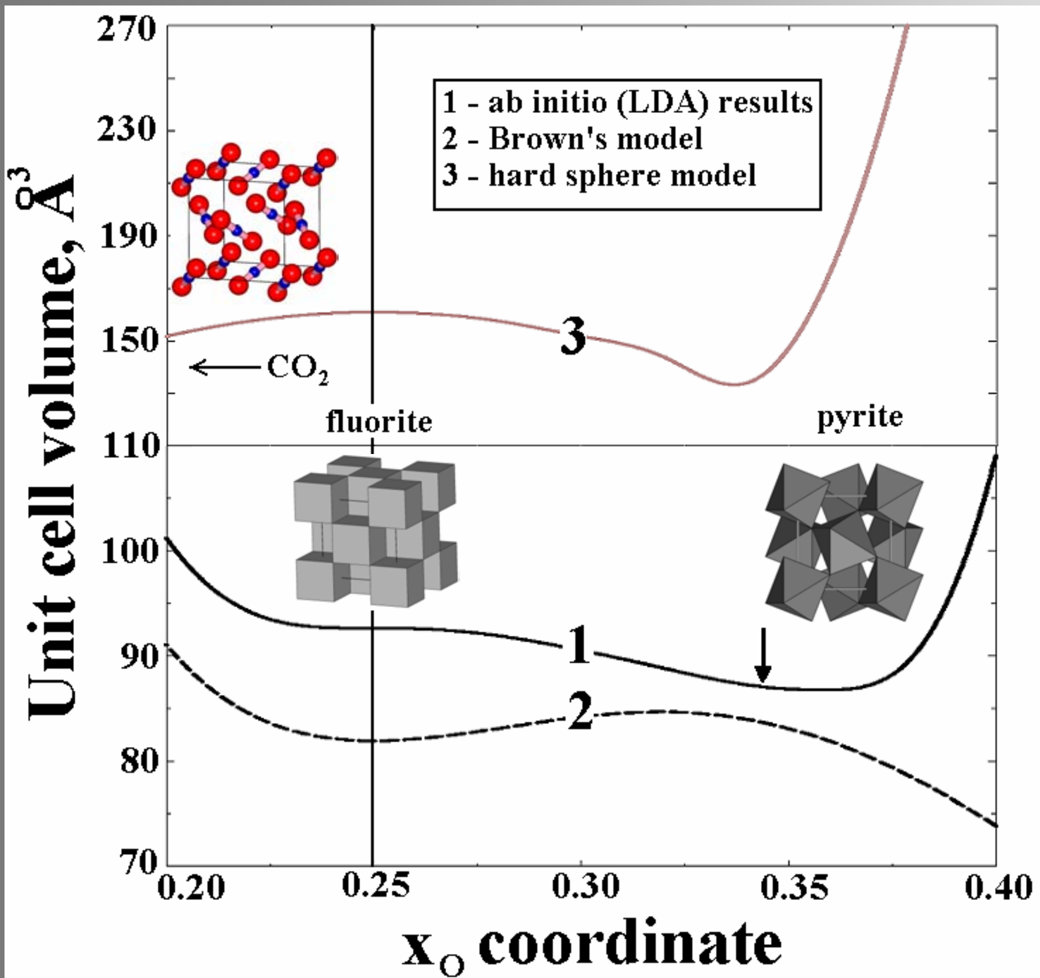
Oganov et al., Submitted to PRL (2004)

- No seismic discontinuities from SiO_2 transitions.
- Breakdown of close packing at >200 GPa!



Pyrite-type structure (210 GPa<P)

Breakdown of Close Packing



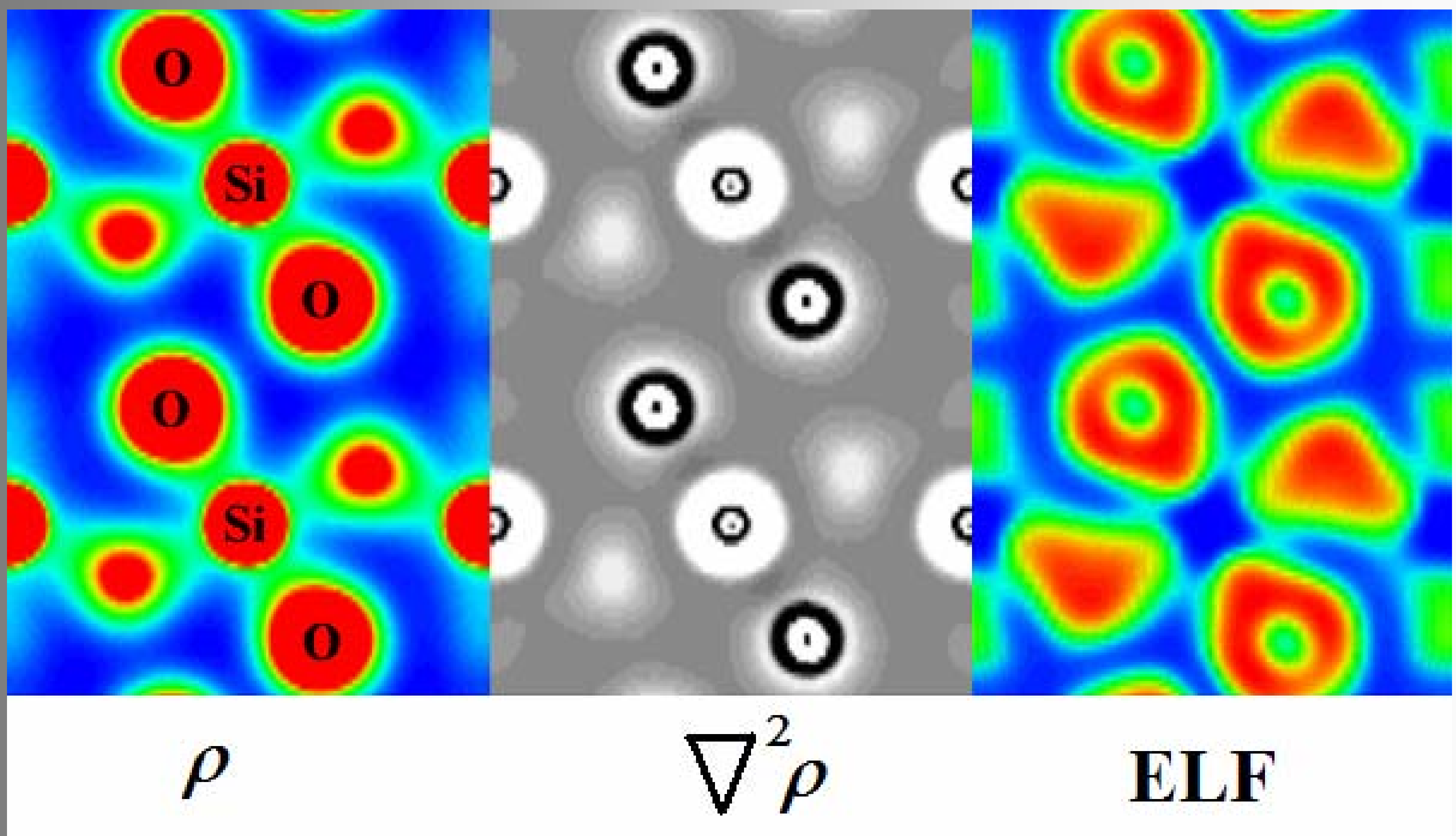
From Oganov et al., submitted to PRL (2004).

- Atoms don’t behave as spheres!
- Non-close-packed

structures far denser!

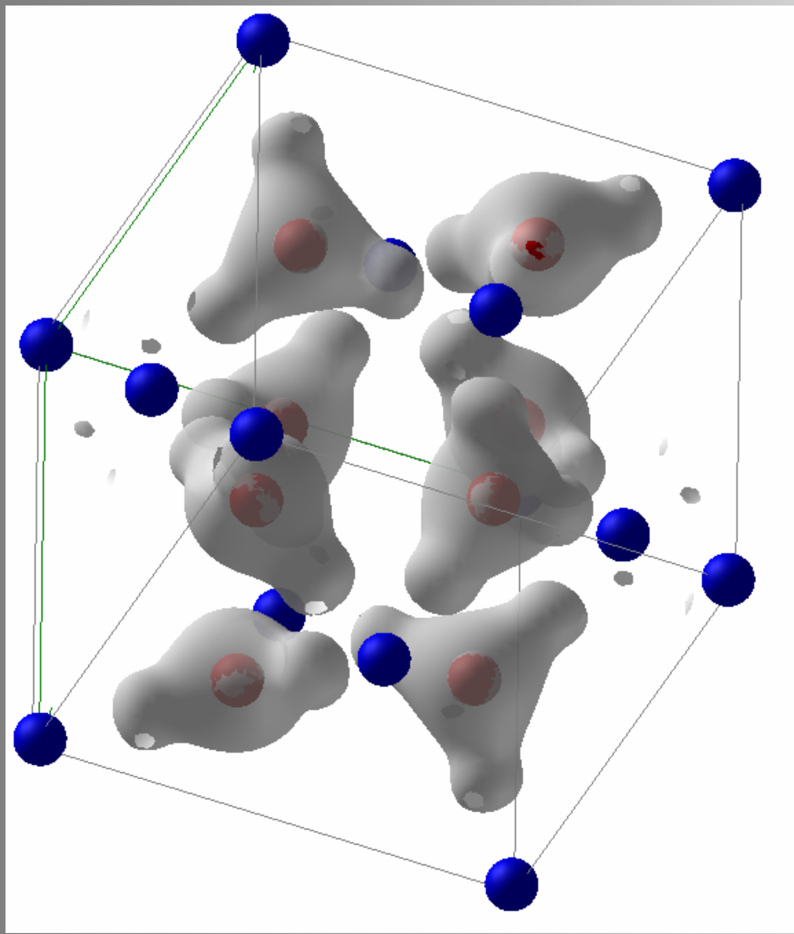
Seeing Atoms and Bonds

- Aspherical atoms.
- No O-O bonds, despite (3,-1) critical points.
- Si charge: +3.17 (Bader), +4.02 (Born).



Oganov et al., submitted to PRL (2004).

Localised Orbital Locator



- Schmider & Becke (2000,2002).
- Own implementation in VASP.

Story 3: $MgSiO_3$ perovskite

Perovskite crystals ($CaTiO_3$)

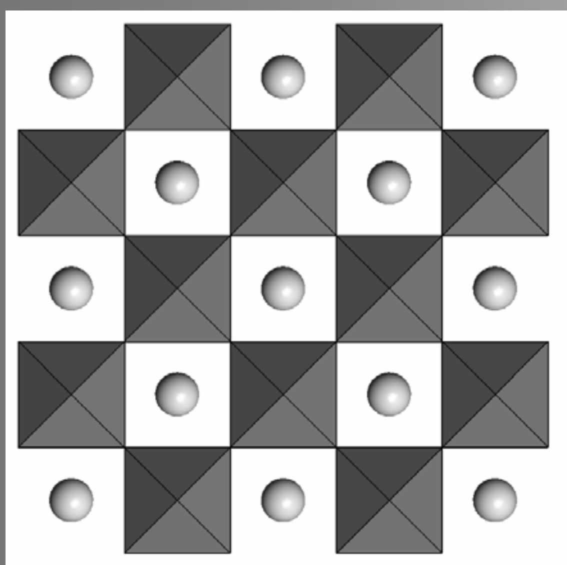
- $(Mg,Fe)SiO_3$ perovskite ~40 vol.% of the Earth.

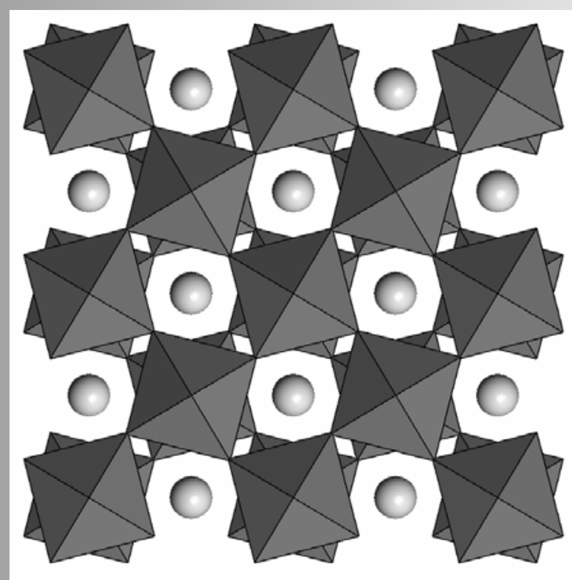
Three issues:

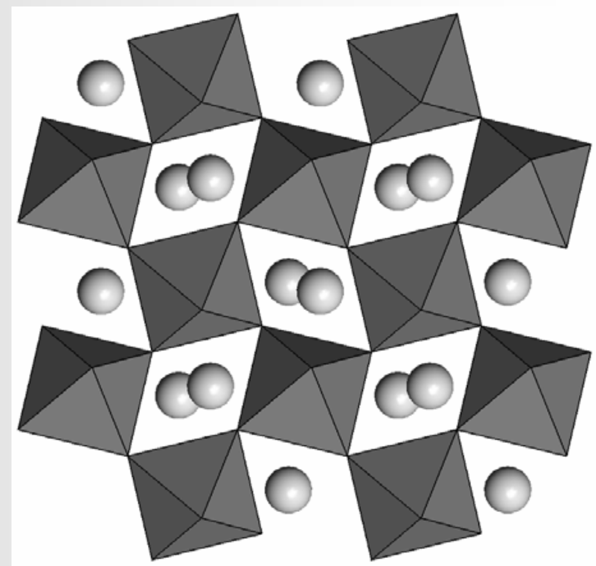
- **Symmetry of perovskite**
- **Decomposition of perovskite**
- **Post-perovskite phase**

1. Symmetry

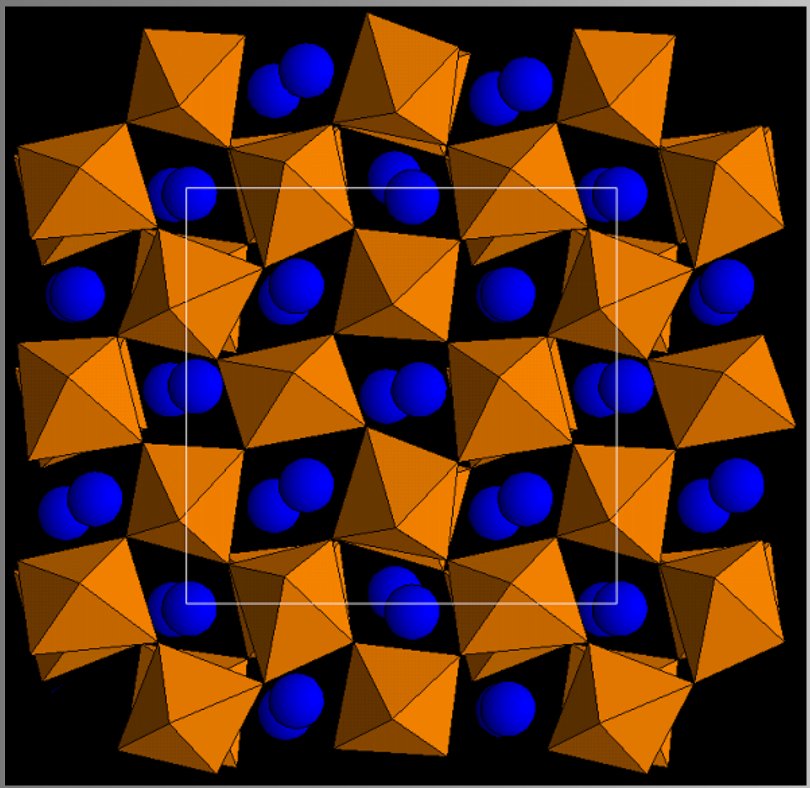
- Ideal structure – cubic (*Pm3m*).
- $MgSiO_3$ perovskite at ambient conditions – *Pbnm*.
- Higher symmetry at high *P*-*T* ?

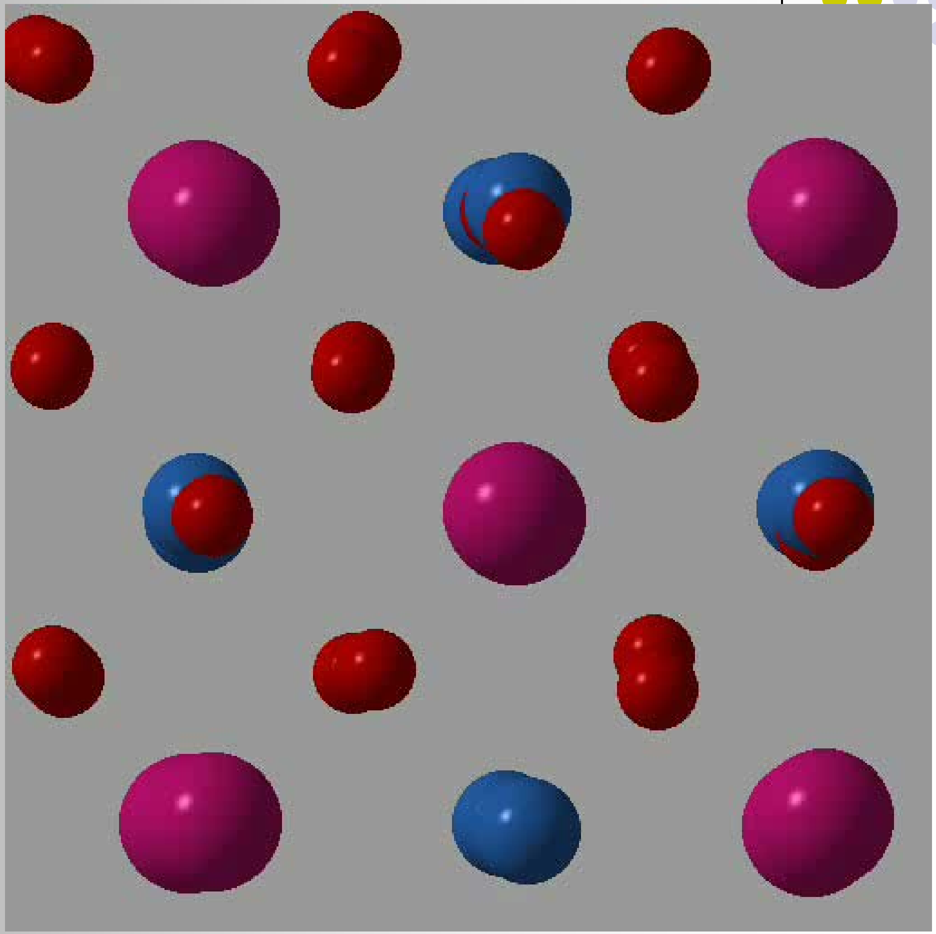

Cubic (*Pm*3*m*)


Tetragonal (*I*4/*mcm*)


Orthorhombic (*Pbnm*)

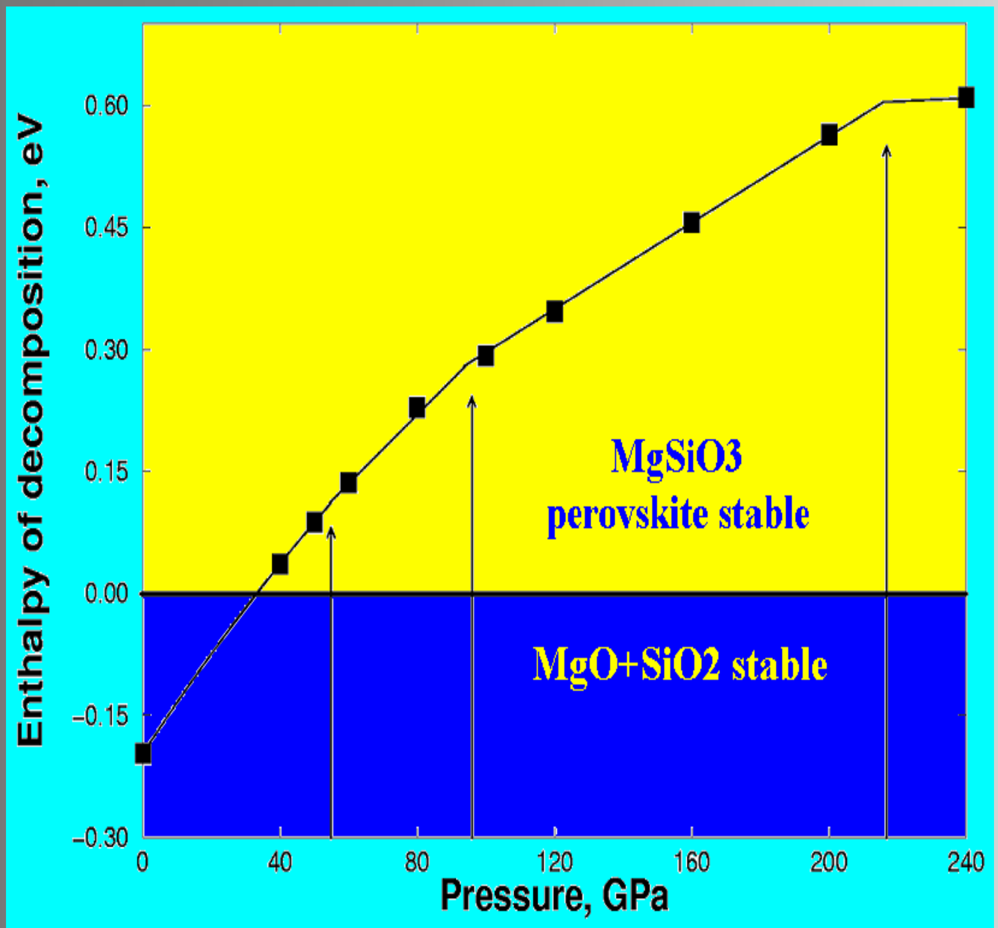
1. Symmetry





$MgSiO_3$ perovskite at 88 GPa and 3500 K

$MgSiO_3$: decomposition



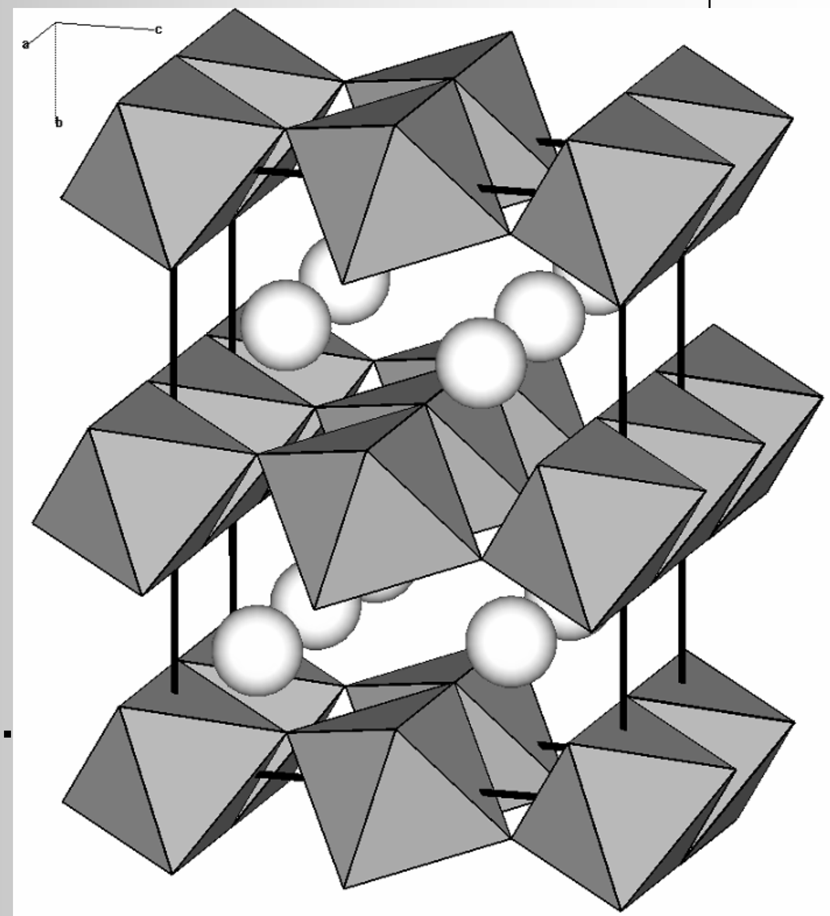
Enthalpy of decomposition of $MgSiO_3$ perovskite. Oganov et al., In prep. (2004)

- Decomposition at high-*P*-*T*?
- Theory: NO!
- ΔS=-5 Jmol^{-1}K^{-1} (100 GPa, 3000 K).

$MgSiO_3$: Post-perovskite phase

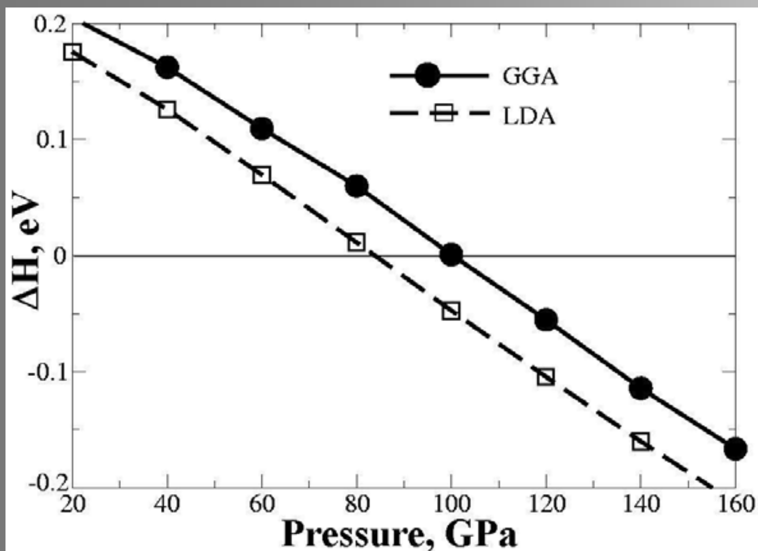
- S.Ono (2004): proposed that $MgSiO_3$ could adopt Fe_2O_3-III structure.
- Post-perovskite phase

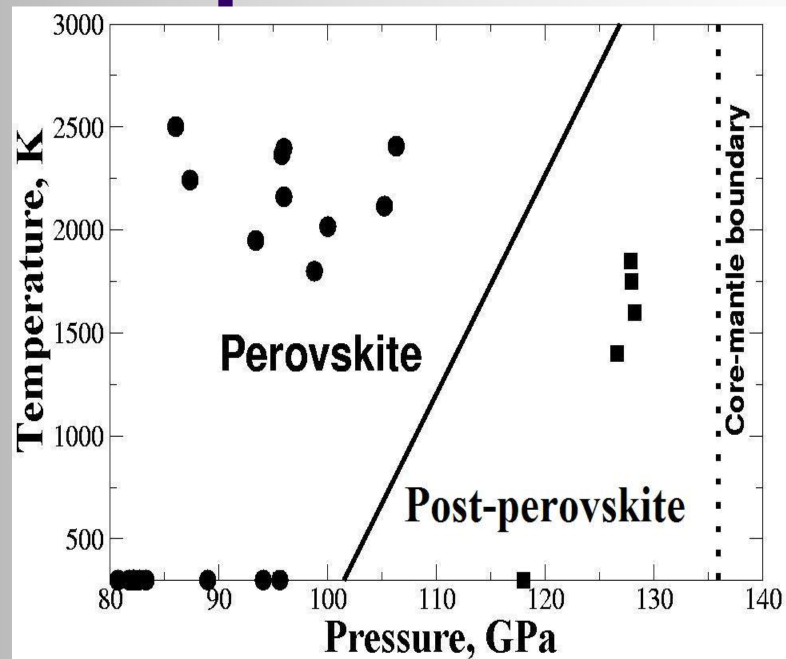
  ~75 vol.% of D'' layer!
- Experimentally confirmed by Oganov & Ono (2004) and Murakami et al. (2004).

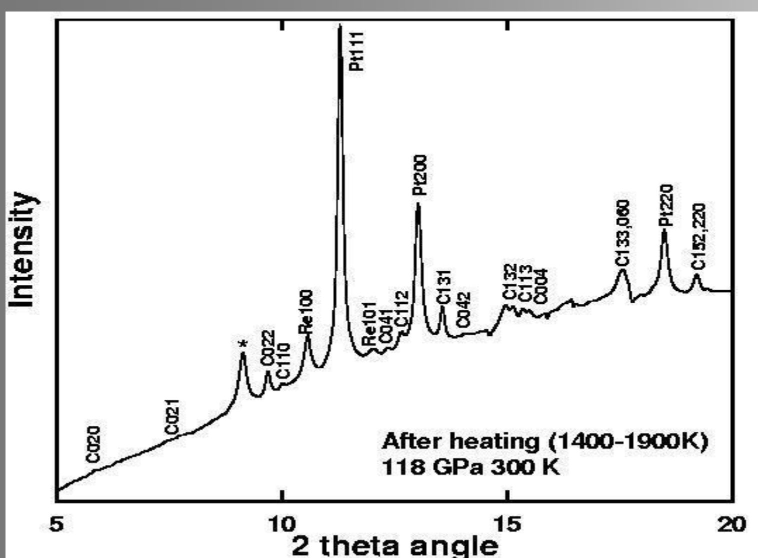


Structure of post-perovskite phase of $MgSiO_3$.
(Oganov & Ono, subm. to Nature, 2004).

Predictions and Experiment







Exp.:	PAW-GGA:
a = 2.471(4) Å, b = 8.091(12) Å, c = 6.110(11) Å	a = 2.474 Å, b = 8.121 Å, c = 6.138 Å
Space group *Cmcm*	

Elastic Constants of Post-perovskite

Table 3. Elastic constants of perovskite and post-perovskite at 120 GPa*.

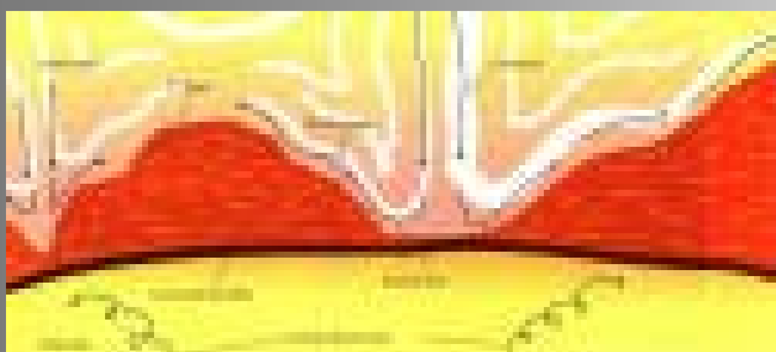
	C_{11}	C_{22}	C_{33}	C_{12}	C_{13}	C_{23}	C_{44}	C_{55}	C_{66}	K	G
Perovskite	907	1157	1104	513	406	431	364	271	333	648.0	310.9
	Acoustic velocities: v_p=14118, v_s=7636, v_ϕ=11026 m/s										
Post-perovskite	1252	929	1233	414	325	478	277	266	408	647.2	327.5
	Acoustic velocities: v_p=14158, v_s=7783, v_ϕ=10940 m/s										

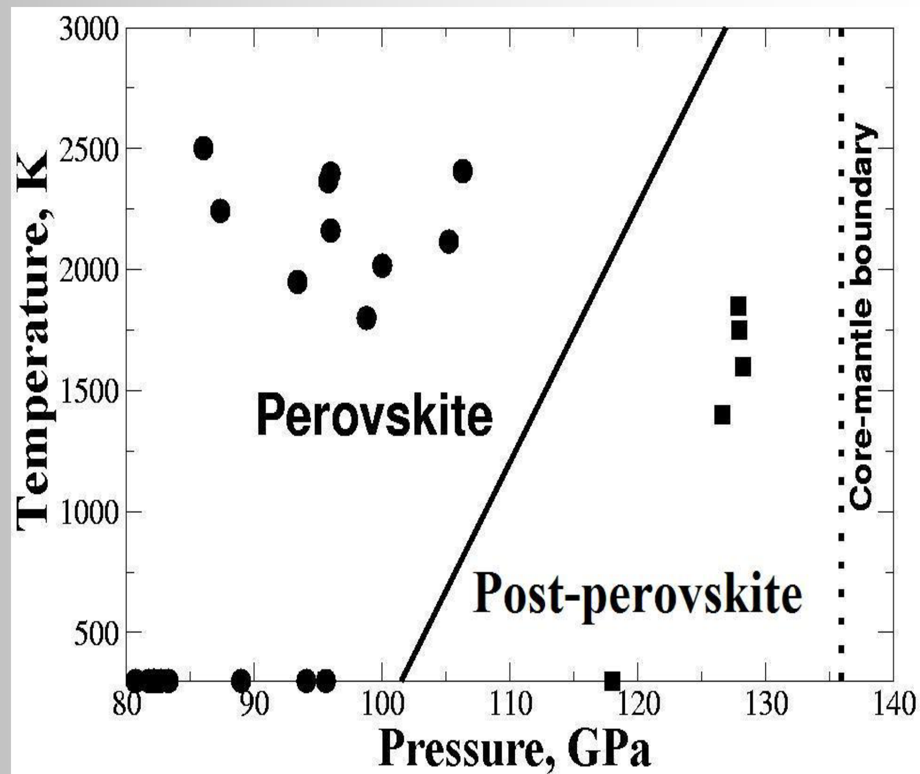
*GGA results. All elastic constants are in GPa.

- VASP: PAW-GGA calculations using stress-strain relations.
- Similar to ABINIT result using D.R. Hamann’s method (when stress state is taken into account).
- Explain most of the D’’ mysteries!

$MgSiO_3$: Post-perovskite phase

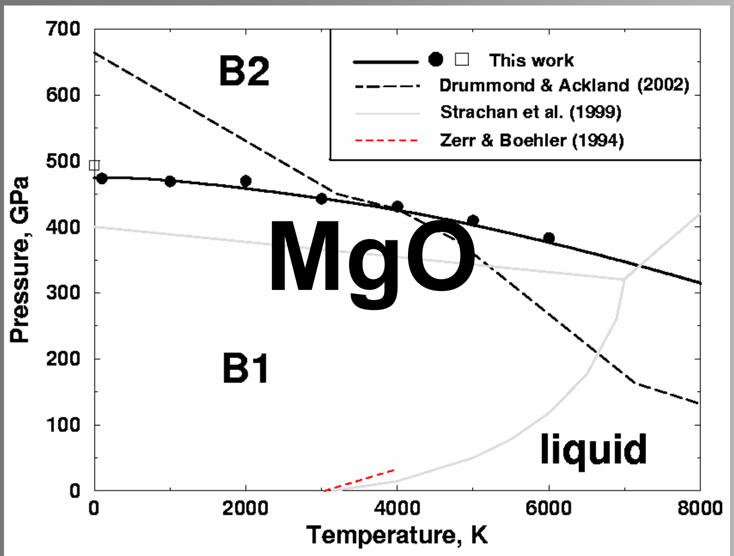
- Matches D'' discontinuity: 2740 km depth, 1.4% jump in v_s, strong topography.
- Explains seismic anisotropy of D'' and its other enigmas.
- D'' evolves with time.

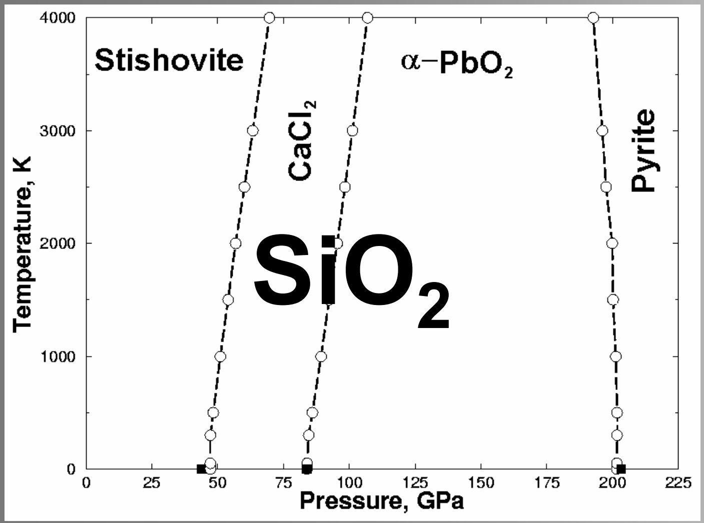


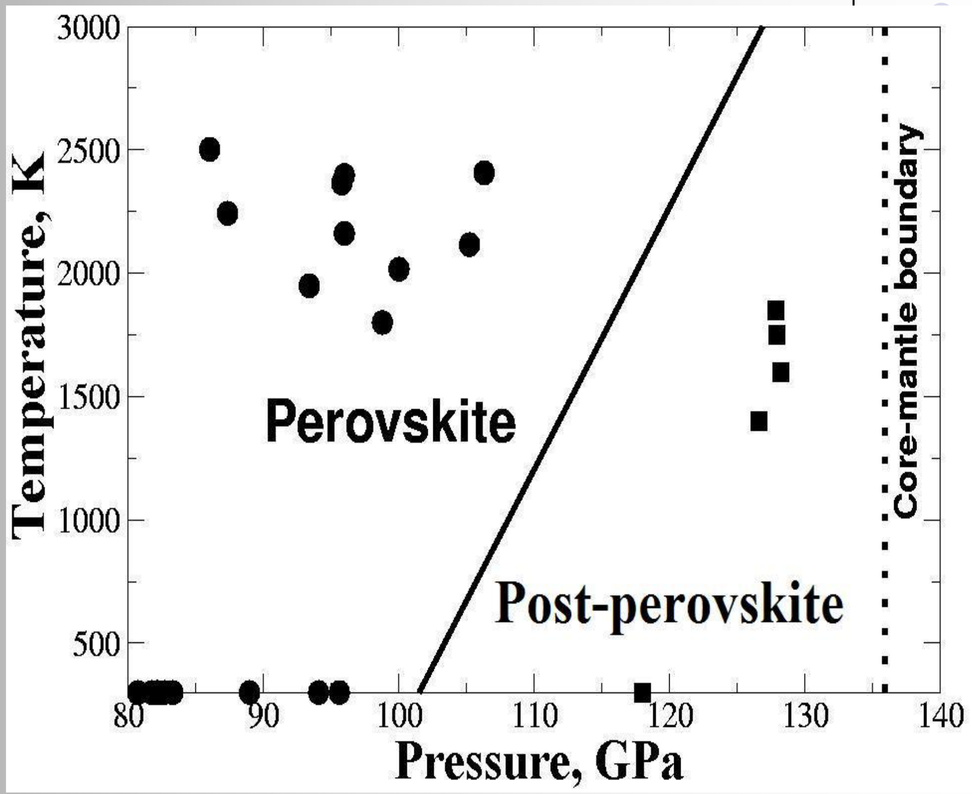


Theoretical and experimental phase diagram of $MgSiO_3$.

Summary







MgSiO$_3$

Further Work and Challenges

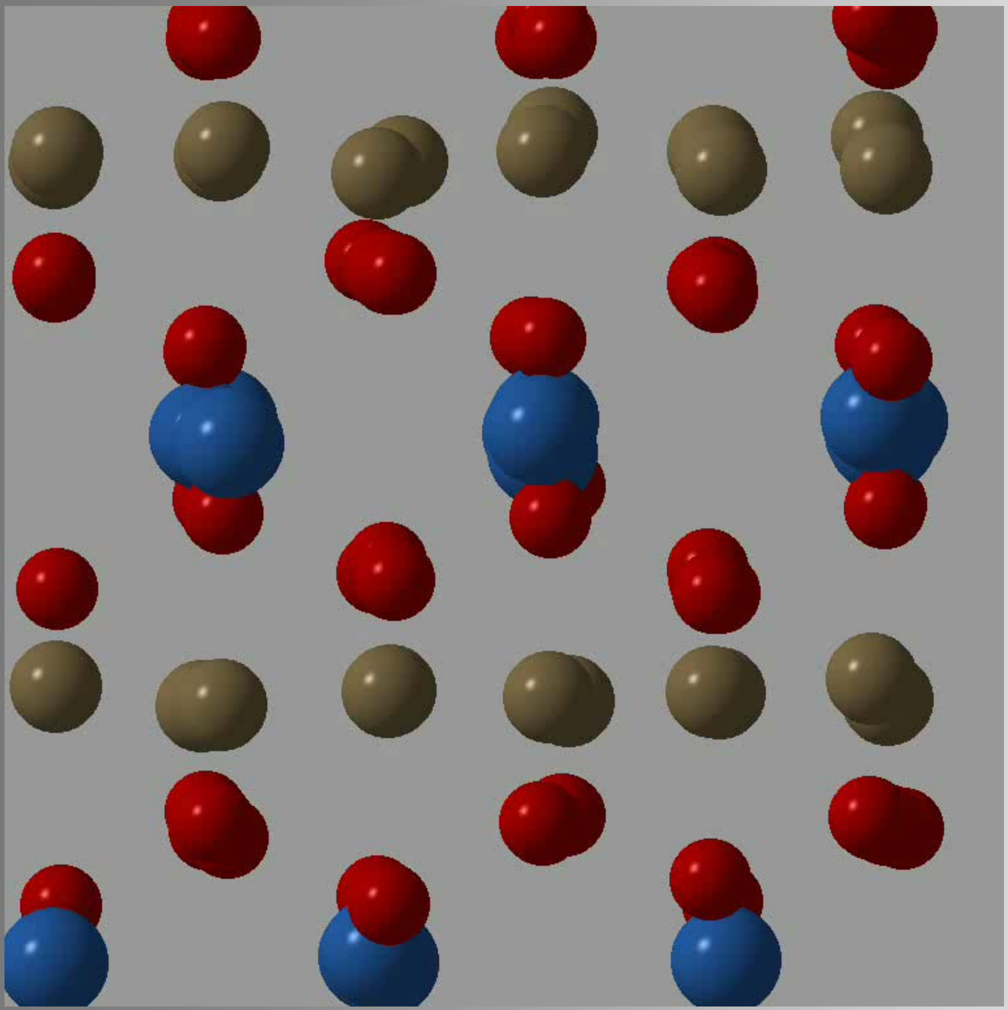
- Structure prediction – Genetic Algorithms?
- Solid solutions (Monte Carlo?).
- Strongly correlated systems – (Mg,Fe)O etc.

Appendix I. Accuracy.

- **MgO, 1 atm, 300 K:**
- Cv=36.58/36.87 theory/exp.
- S =26.81/27.13

- **Stishovite (SiO_2), 1 atm, 300 K**:
- Cv=41.3/42.2 theory/exp.
- S = 24.6/25.9

Appendix II. MD & visualisation



- 120-atom cell.
- PAW, GGA.
- VASP.

- Movie – STM3 (thanks to M.Valle & J.Favre)
- Compatible with CPMD, VASP and DL_POLY formats.
- ABINIT

Appendix III. Elasticity under pressure

- Non-uniqueness of the definition (strain type, differentiation details) when pressure (*P*) is present.

Most useful definition of elastic constants:

$$\sigma_{ij} = C_{ijkl}\,\eta_{kl}\,, \qquad \{1\}$$

Usual definition of strain: $$a_{ij}' = (\delta_{ij} + \eta_{ij})\,a_{ij}^{0} \qquad \{2\}$$

$$C^{S}_{ijkl} = \frac{1}{V}\left(\frac{\partial^2 H}{\partial \eta_{ij}\partial \eta_{kl}}\right)_S = \frac{1}{V}\left(\frac{\partial^2 E}{\partial \eta_{ij}\partial \eta_{kl}}\right)_S + \frac{P}{2}\left(2\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk} - \delta_{jl}\delta_{ik}\right) \qquad \{3\}$$

ABINIT calculates $\frac{1}{V}\frac{\partial}{\partial \eta_{11}}(V\sigma_{11})$

Example: $$C_{11} = \frac{1}{V}\left(\frac{\partial^2 E}{\partial \eta_{11}\partial \eta_{11}}\right)_S = \frac{1}{V}\frac{\partial}{\partial \eta_{11}}(V\sigma_{11}) + P \qquad \{4\}$$