Pressure—Volume—Temperature Equation of State

S.-H. Dan Shim (심상헌)

ASU School of Earth & Space Exploration
Arizona State University

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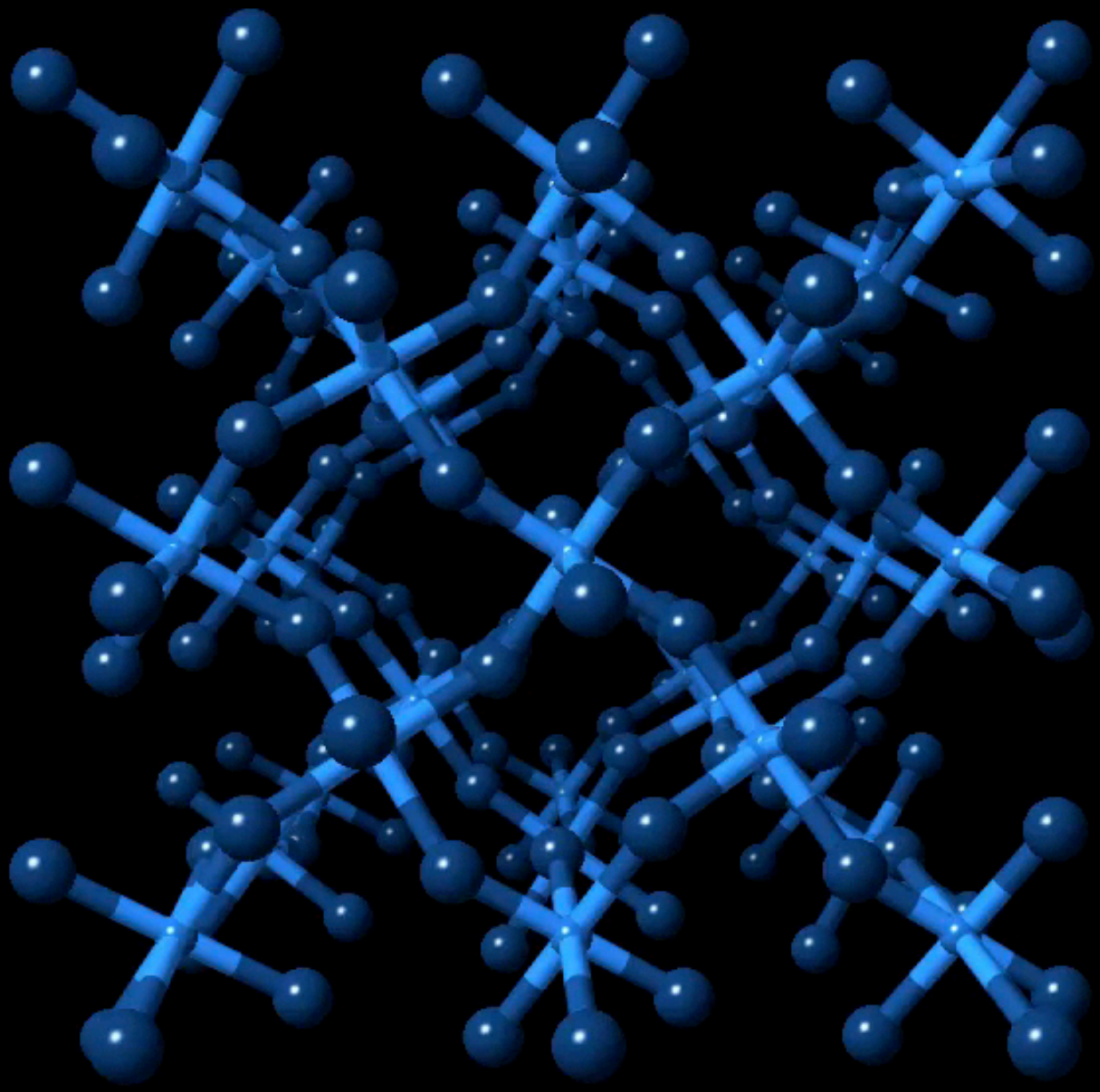


Equations relating state variables (pressure, temperature, volume, or energy).

$$f(P, V, T) = 0$$

- Backgrounds
- Equations
- Limitations
- Applications

Ideal Gas Law

$$PV = nRT$$

Ideal Gas Law

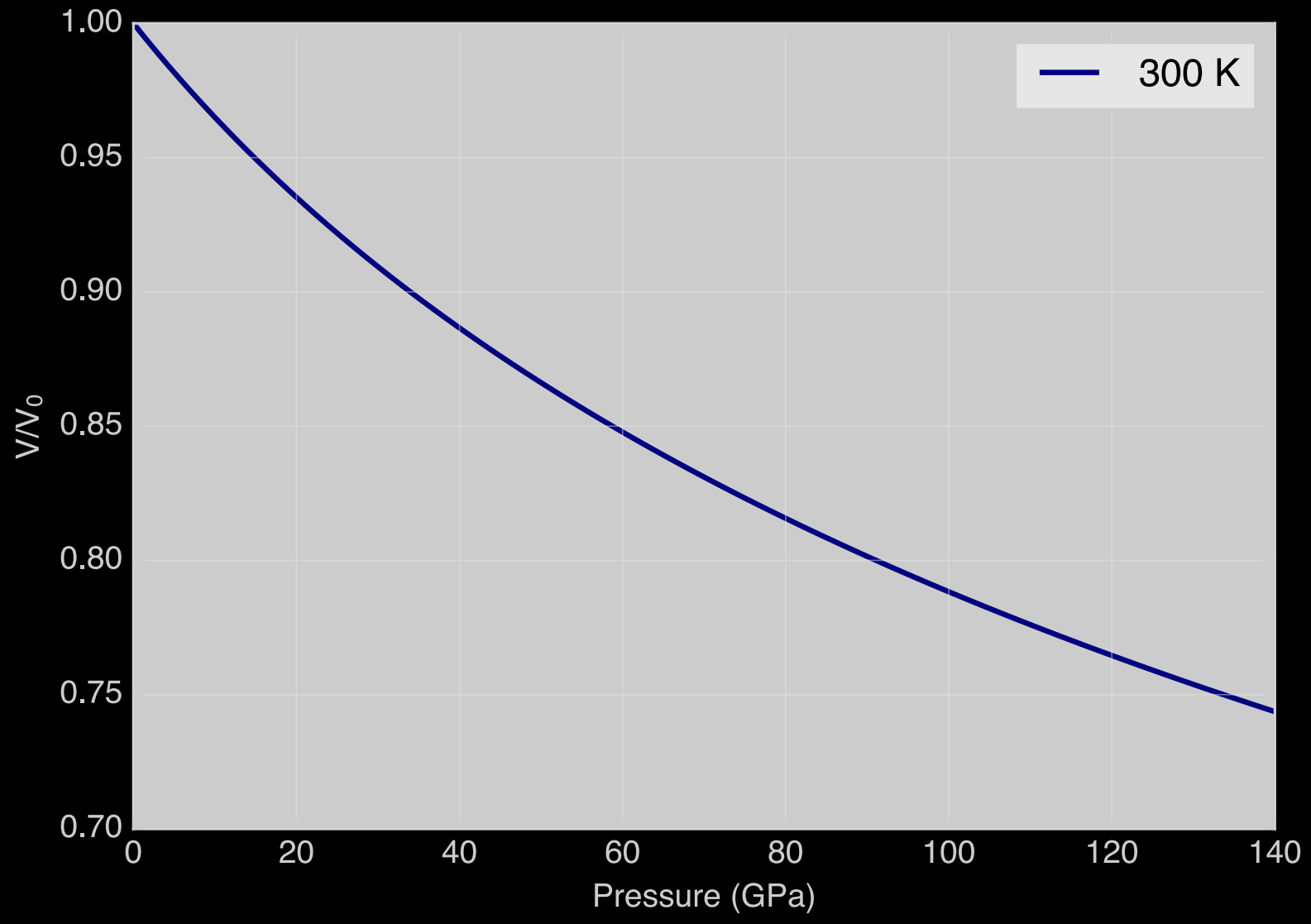
- Volume increases with temperature
- Volume decreases with pressure
- Pressure increases with temperature

$$PV = nRT$$

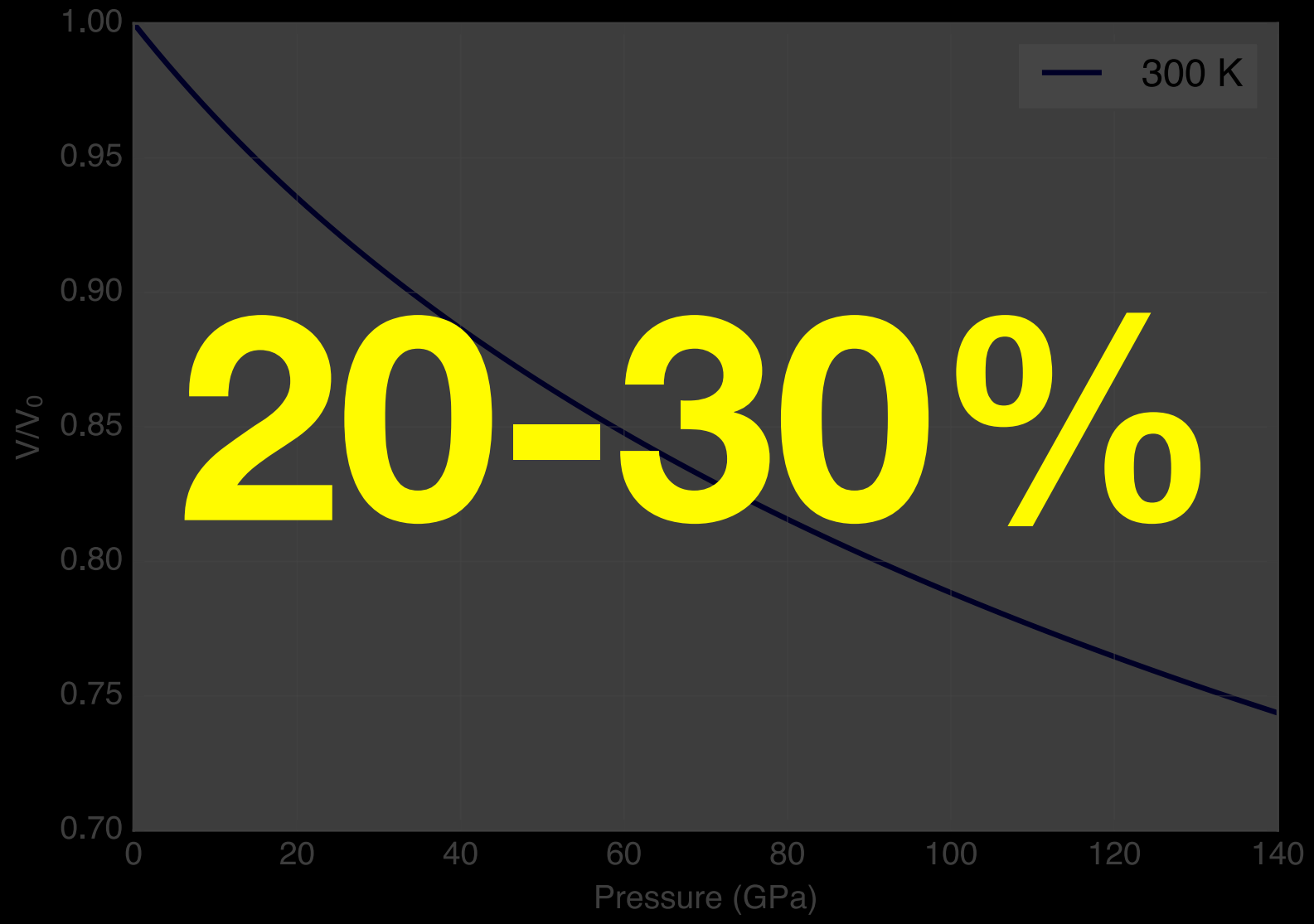
Stress (σ) and Strain (ϵ)

$$\sigma_{ij} = C_{ijkl}\epsilon_{kl},$$

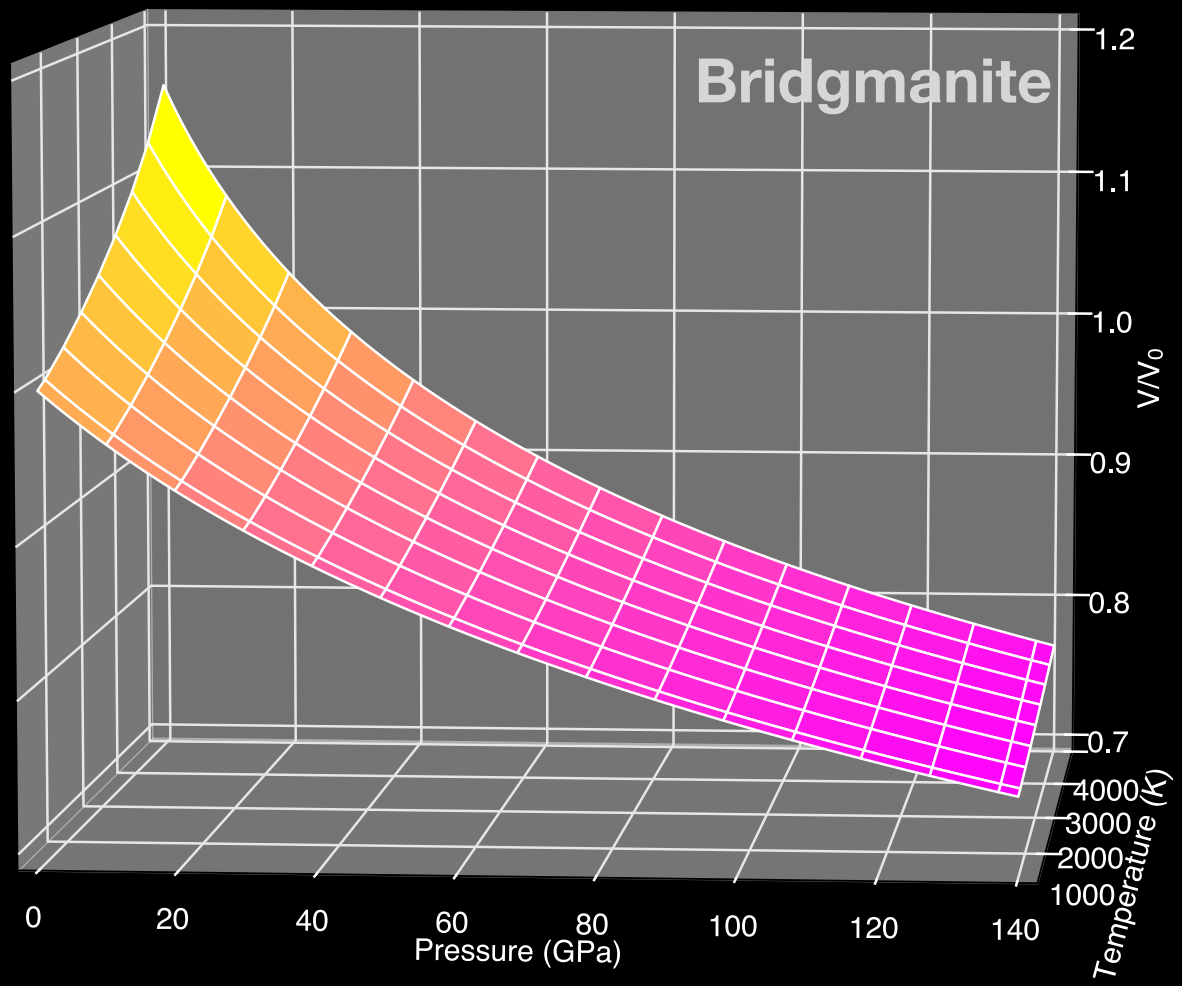
Bridgmanite in the Mantle



Strain in the Mantle



$P-V-T$ EOS


Bridgmanite
1.2
1.1
1.0
0.9
0.8
0.7
V/V0
4000
3000
2000
1000
Temperature (K)
0
20
40
60
80
100
120
140
Pressure (GPa)

Energy

$$dU = TdS - PdV,$$

$$dH = TdS + VdP,$$

$$dF = -SdT - PdV,$$

$$dG = -SdT + VdP.$$

A Few Terms to Remember

- Isothermal
- Isobaric
- Isochoric
- Isentropic
- Adiabatic

Energy

$$dU = TdS - PdV,$$

$$dH = TdS + VdP,$$

$$dF = -SdT - PdV,$$

$$dG = -SdT + VdP.$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P,$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial G}{\partial T}\right)_P,$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_S = -\left(\frac{\partial F}{\partial V}\right)_T,$$

$$V = \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T.$$

Thermodynamic Parameters

Isothermal bulk modulus

$$K_T = -V\left(\frac{\partial P}{\partial V}\right)_T = \rho\left(\frac{\partial P}{\partial \rho}\right)_T = V\left(\frac{\partial^2 F}{\partial V^2}\right)_T.$$

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Thermal expansion parameter

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P.$$

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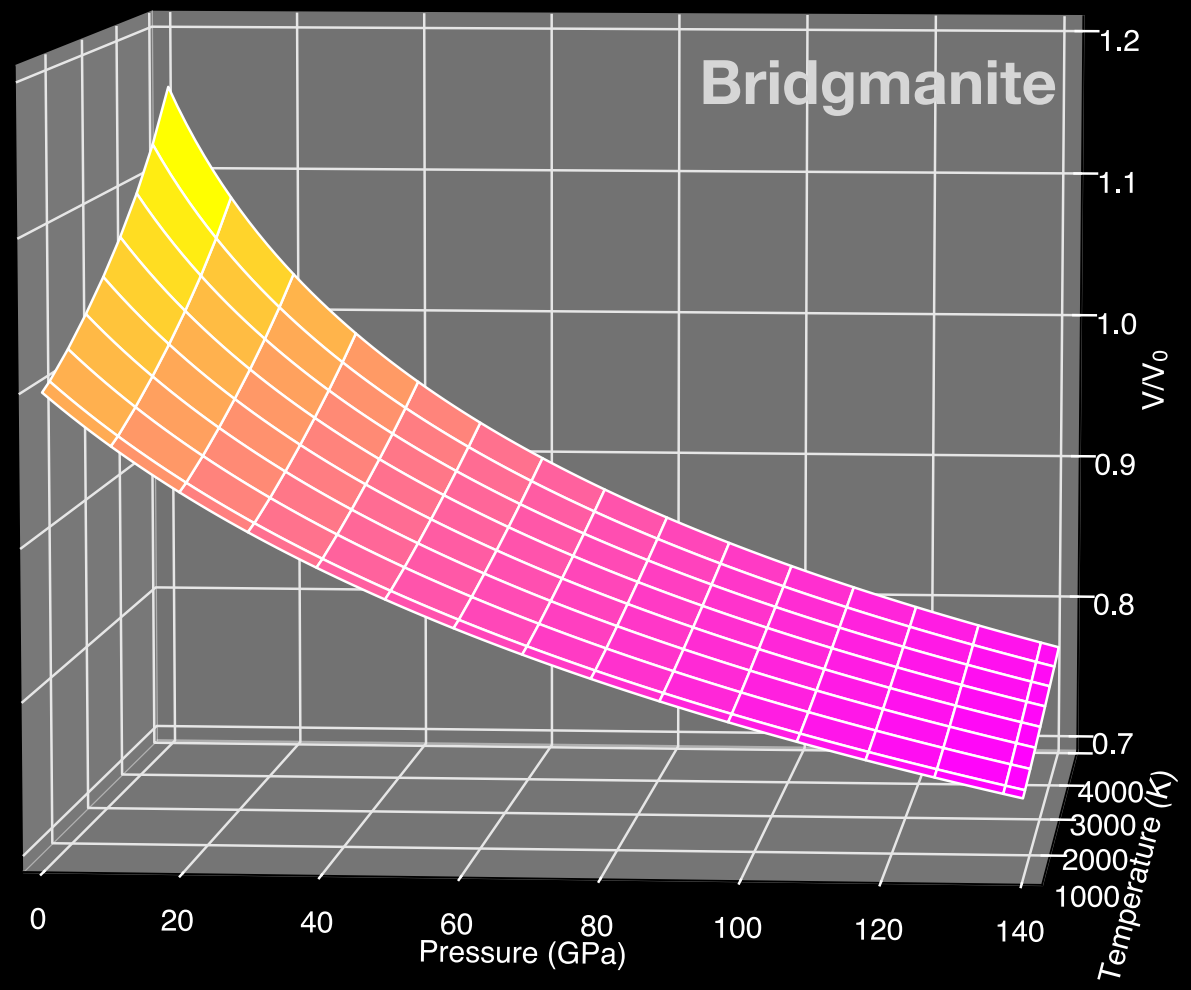
Grüneisen parameter

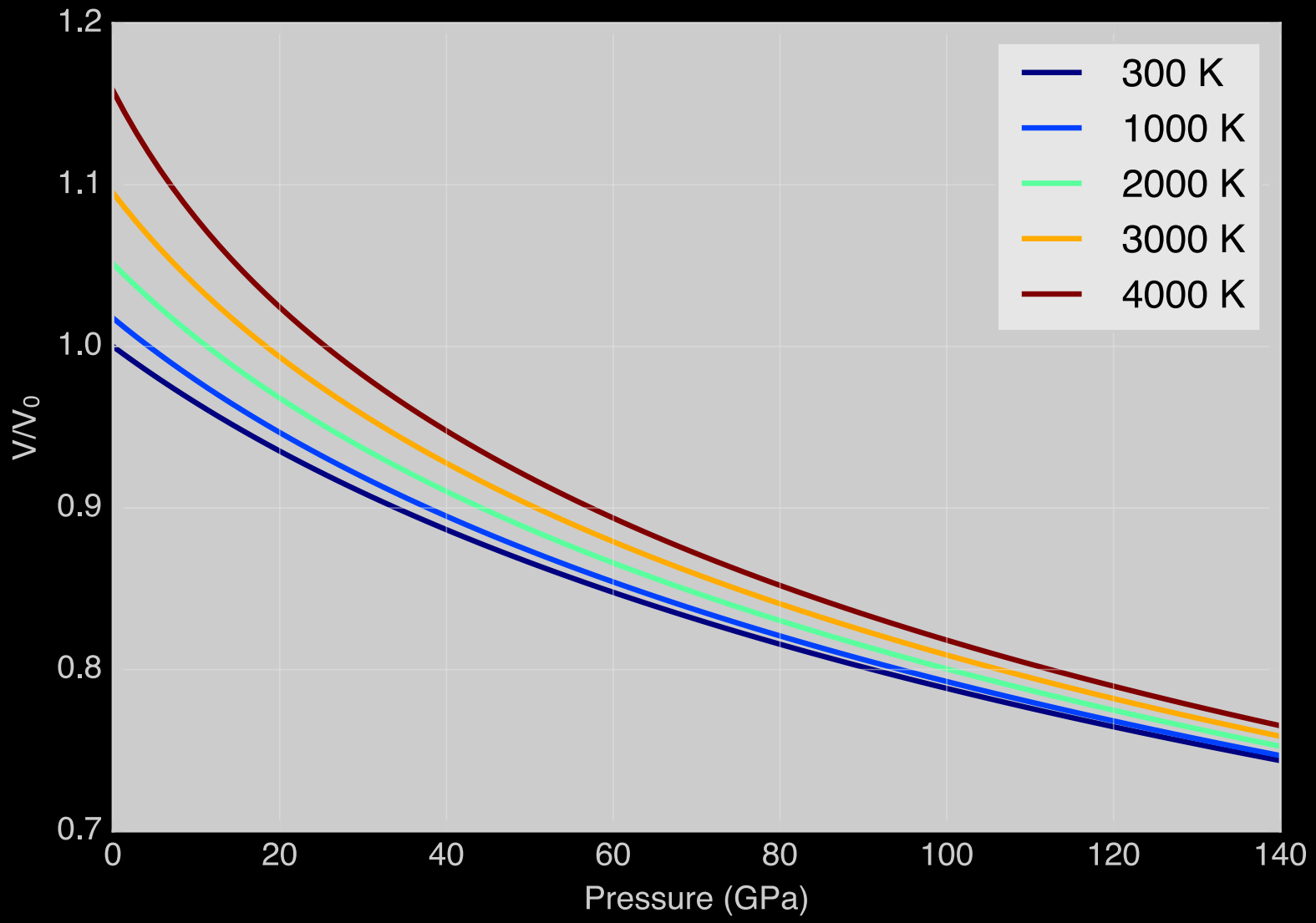
$$\gamma = V\left(\frac{\partial P}{\partial U}\right)_V = \frac{1}{\rho C_V}\left(\frac{\partial P}{\partial T}\right)_V$$

$P-V-T$ of EOS

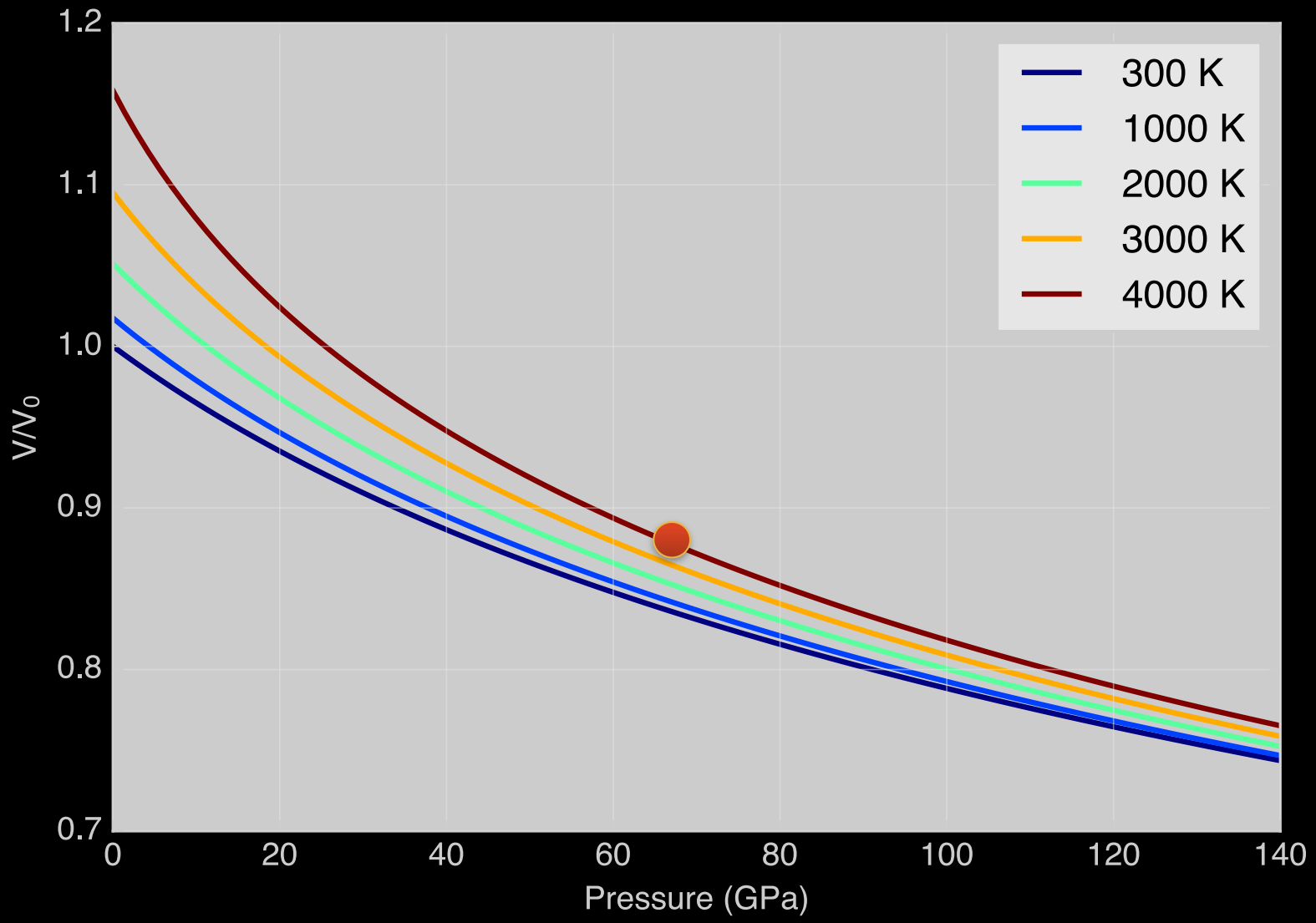
- K_T
- α
- γ



$P-V-T$ EOS


1.2
1.1
1.0
0.9
0.8
0.7
V/V0
0
20
40
60
80
100
120
140
Pressure (GPa)
300 K
1000 K
2000 K
3000 K
4000 K

Shape of EOS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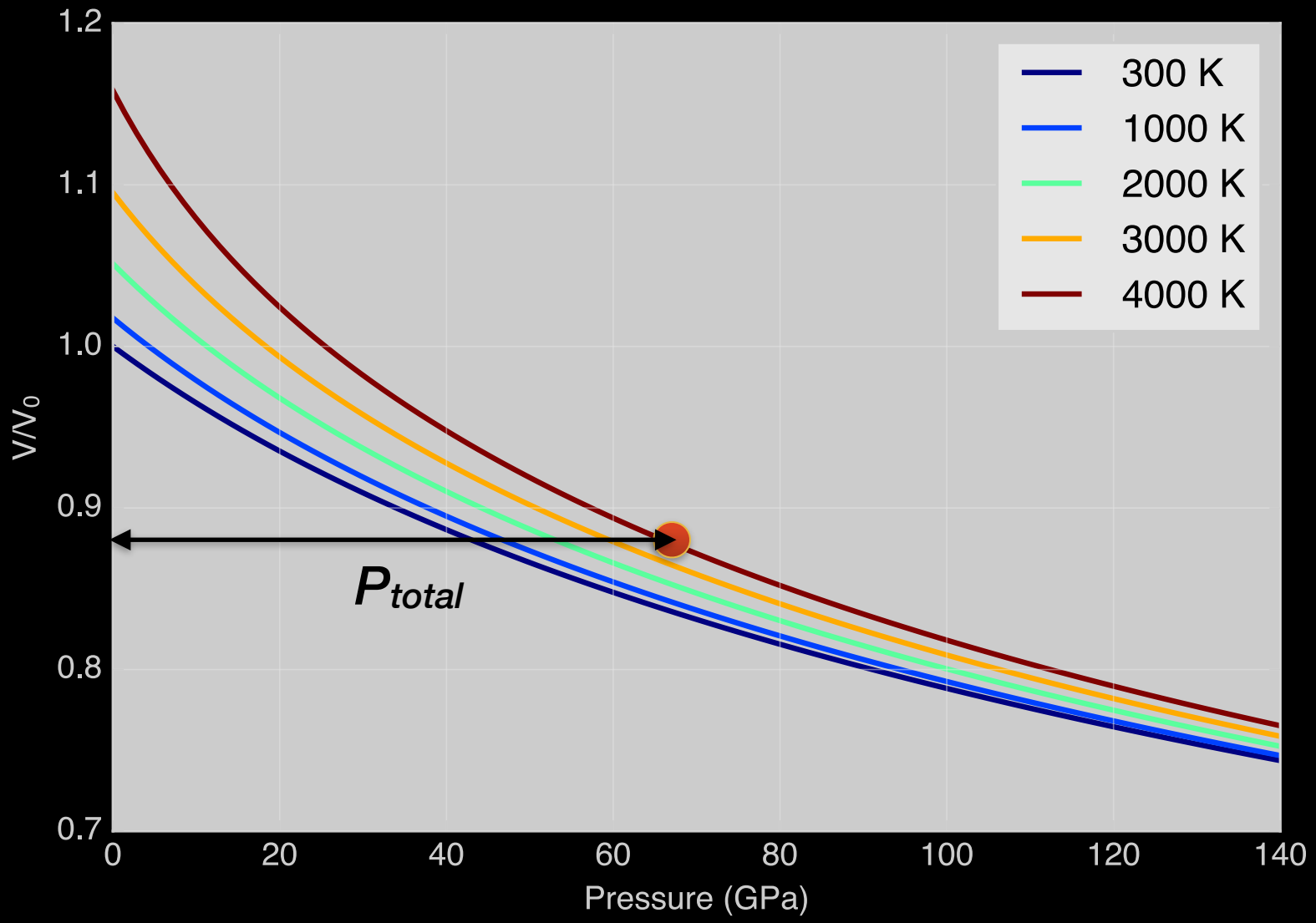
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2000 K
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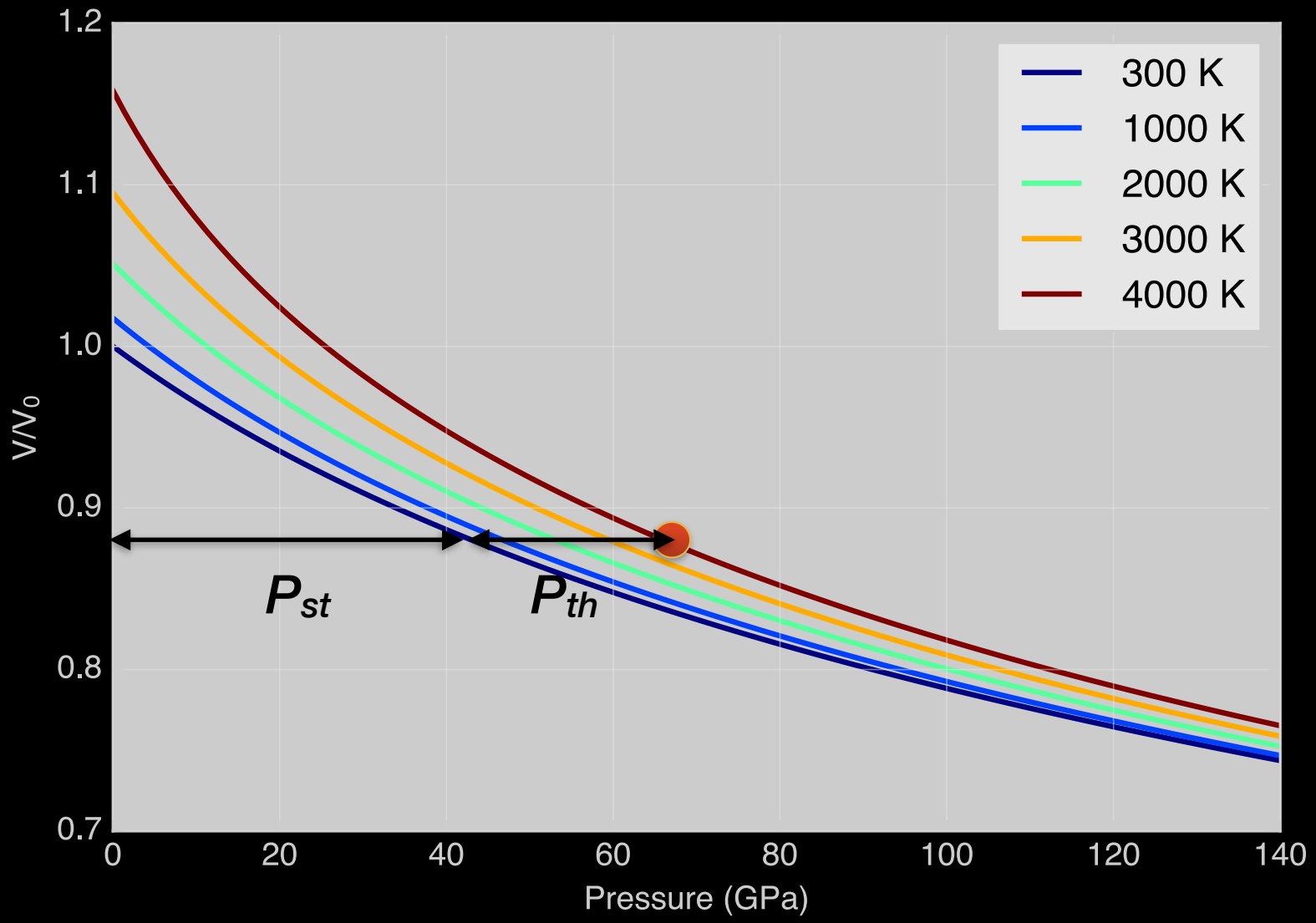
4000 K
Ptotal

Shape of EOS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Pressure (GPa)
300 K
1000 K
2000 K
3000 K
4000 K
Pst
Pth

Thermal Pressure

$$F_{total} = F_{st} + F_{vib} + F_{elec}$$

$$P(V, T) = P_{st}(V, T_0) + \Delta P_{th}(V, T)$$

Isothermal EOS

$$K = -\frac{dP}{d\ln V} = \frac{dP}{d\ln \rho}$$

$$V = V_0 \exp\left[\frac{-P}{K_0}\right]$$

Assumes that K does not change with P, T

Murnaghan EOS

$$K = K_0 + K_0' P$$

$$K = -\frac{dP}{d\ln V} = \frac{dP}{d\ln \rho}$$

$$\rho = \rho_0 \left(1 + \frac{K_0'}{K_0} P \right)$$

However, K increases nonlinearly with pressure

Birch-Murnaghan EOS

$$F = a + bf + cf^2 + df^3 + \ldots$$

$$\frac{V_0}{V} = (1 + 2f)^{3/2}$$

F : Energy (U or F)

f : Eulerian finite strain

Birch (1978)

Second Order BM EOS

$$F = a + bf + cf^2$$

$$P = 3K_0 f(1+2f)^{5/2} = \frac{3K_0}{2}\left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3}\right]$$

$$K = -V\frac{dP}{dV} = \frac{K_0}{2}\left[7\left(\frac{V_0}{V}\right)^{7/3} - 5\left(\frac{V_0}{V}\right)^{5/3}\right] = K_0(1+7f)(1+2f)^{5/2}$$

Birch (1978)

Third Order BM EOS

$$F = a + bf + cf^2 + df^3$$

$$P = \frac{3K_0}{2}\left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3}\right]\left\{1 - \xi\left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]\right\}$$

$$\xi = \frac{3}{4}(4 - K_0')$$

Birch (1978)

Truncation Problem

$$F = a + bf + cf^2 + df^3 + \ldots$$

$$\frac{V_0}{V} = (1 + 2f)^{3/2}$$

- Higher order terms can be large at high P
- 2nd order BM assumes $K_0' = 4$
- 3rd order BM assumes complex relation among K_0, K_0', and K_0''

Helmholtz Free Energy

$$dF = -SdT - PdV$$

$$P = -\left(\frac{dF}{dV}\right)_T$$

Therefore, knowing the functional form of free energy with respect to volume change is important for EOS.

Vinet EOS

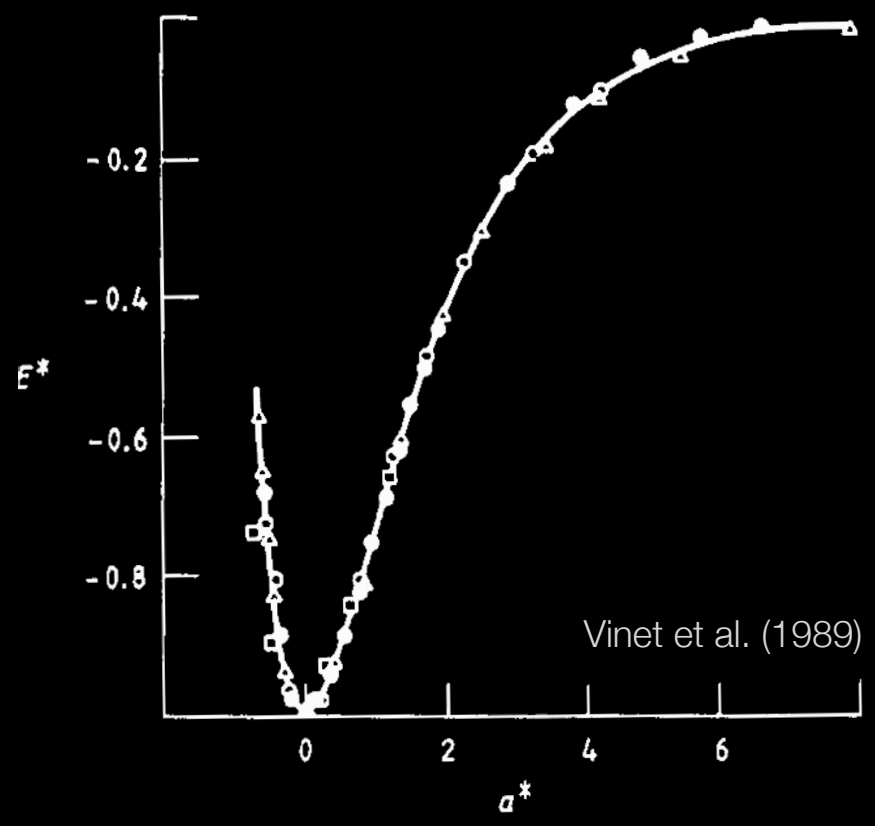


Figure 1. Universal binding energy relation—scaled binding energy (E^*) versus scaled separation (a^*)—for diatomics (●, H_2^+ (molecule)), adhesion (○, Al–Zn (interface)), chemisorption (□, oxygen (chemisorbed)), and cohesion (△, Mo (bulk)).

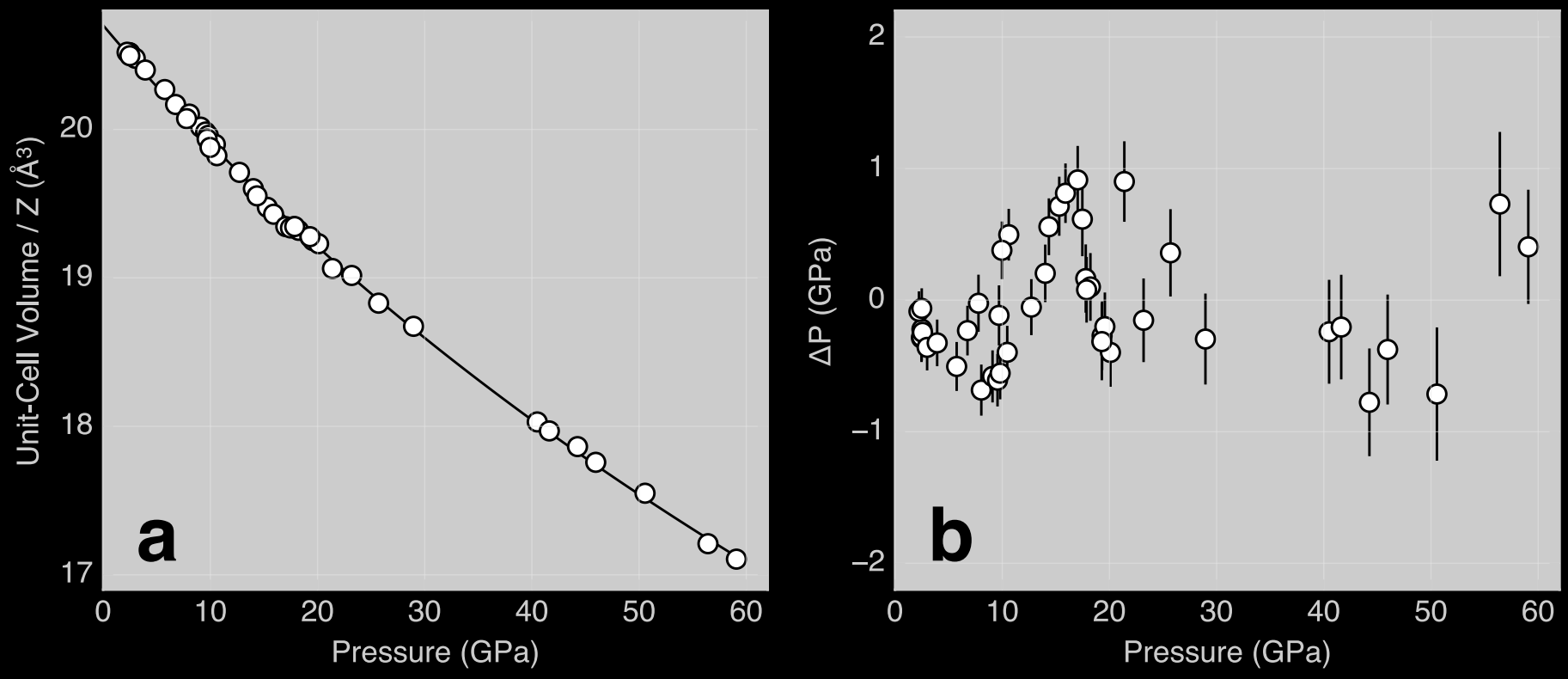
Vinet EOS

$$P = \frac{3K_0(1-x)}{x^2}\exp[\eta(1-x)]$$

$$x = (V/V_0)^{1/3} \qquad \eta = \frac{3}{2}(K_0' - 1)$$

Vinet et al. (1989)

Example: Isotherm Fitting

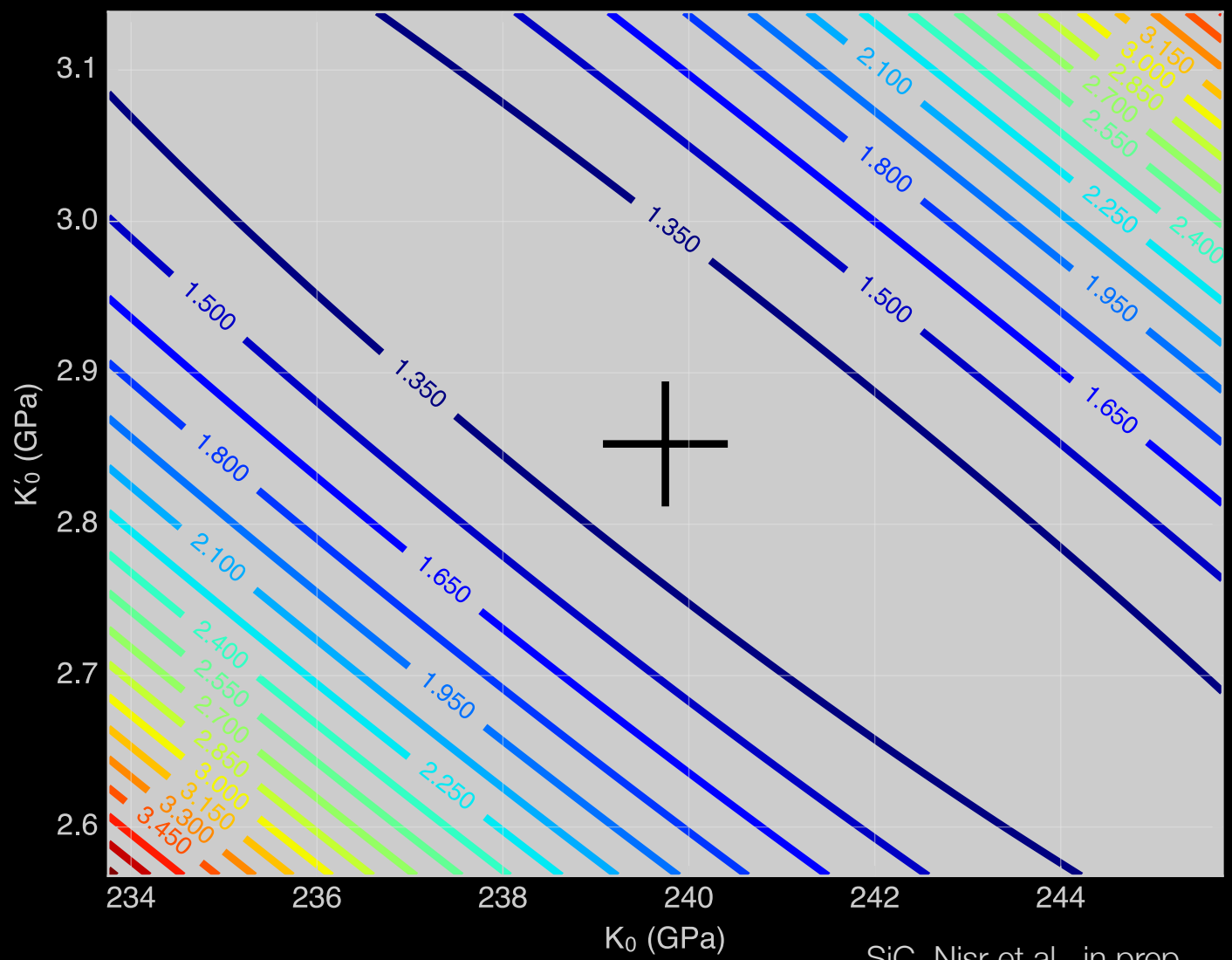


SiC, Nisr et al., in prep.

Parameters to Fit

$$V_0, K_0, K'_0$$

Example: Isotherm Fitting



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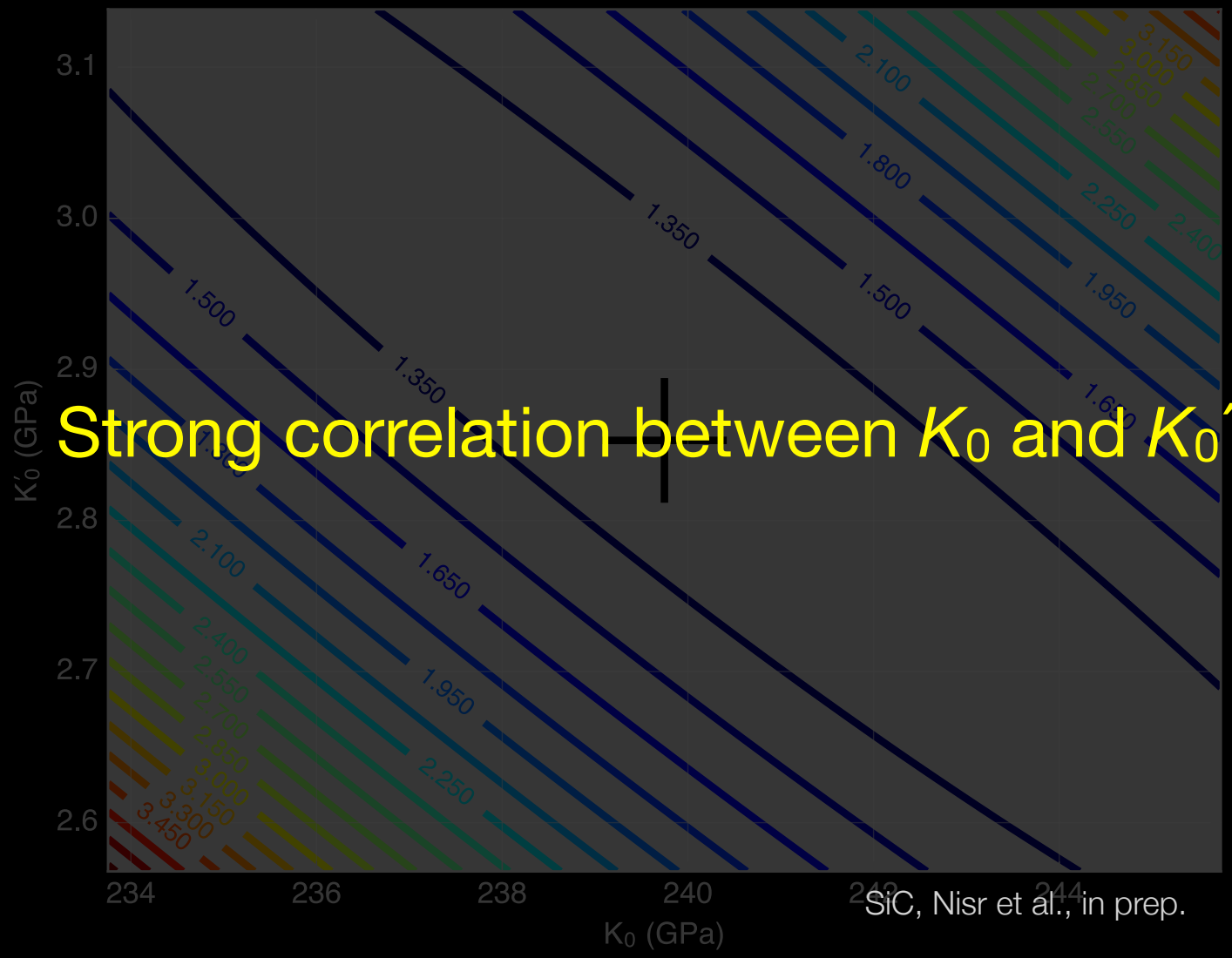

Strong correlation between K_0 and K_0'

SiC, Nisr et al., in prep.

Caution

Table 1. Model parameters for the equations of state of NaCl-B2, Solid Ne, Au, and Pt

Parameters	NaCl-B2*	Ne*	Au†	Pt‡
V_0, Å^3	41.35	88.967	67.850(4)	60.38(1)
K_{0T}, GPa (Vinet)	26.86(2.90)	1.16(14)	167	277
K'_{0T} (Vinet)	5.25(26)	8.23(31)	6.00(2)	5.08(2)
K_{0T}, GPa (B-M)	30.69(2.90)	1.43(14)	167	277
K'_{0T} (B-M)	4.33(26)	8.02(31)	5.77(2)	4.95(2)
θ_0, K	290	75.1	170	230
γ_0,	1.70	2.05	2.97(3)	2.72(3)
q_0	0.5(3)	0.6(3)	0.6(3)	0.5(5)

Fei et al. (2007)

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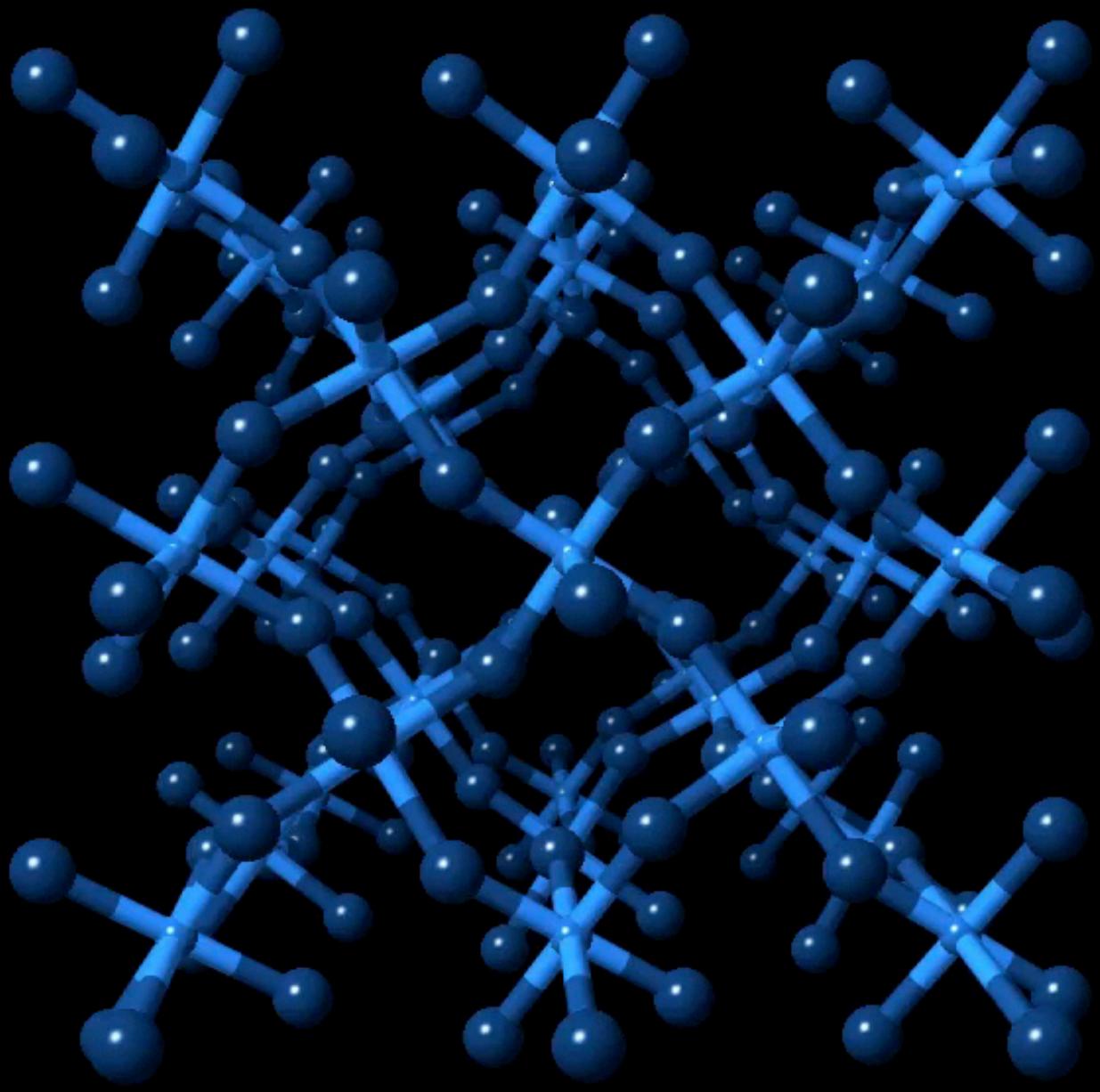
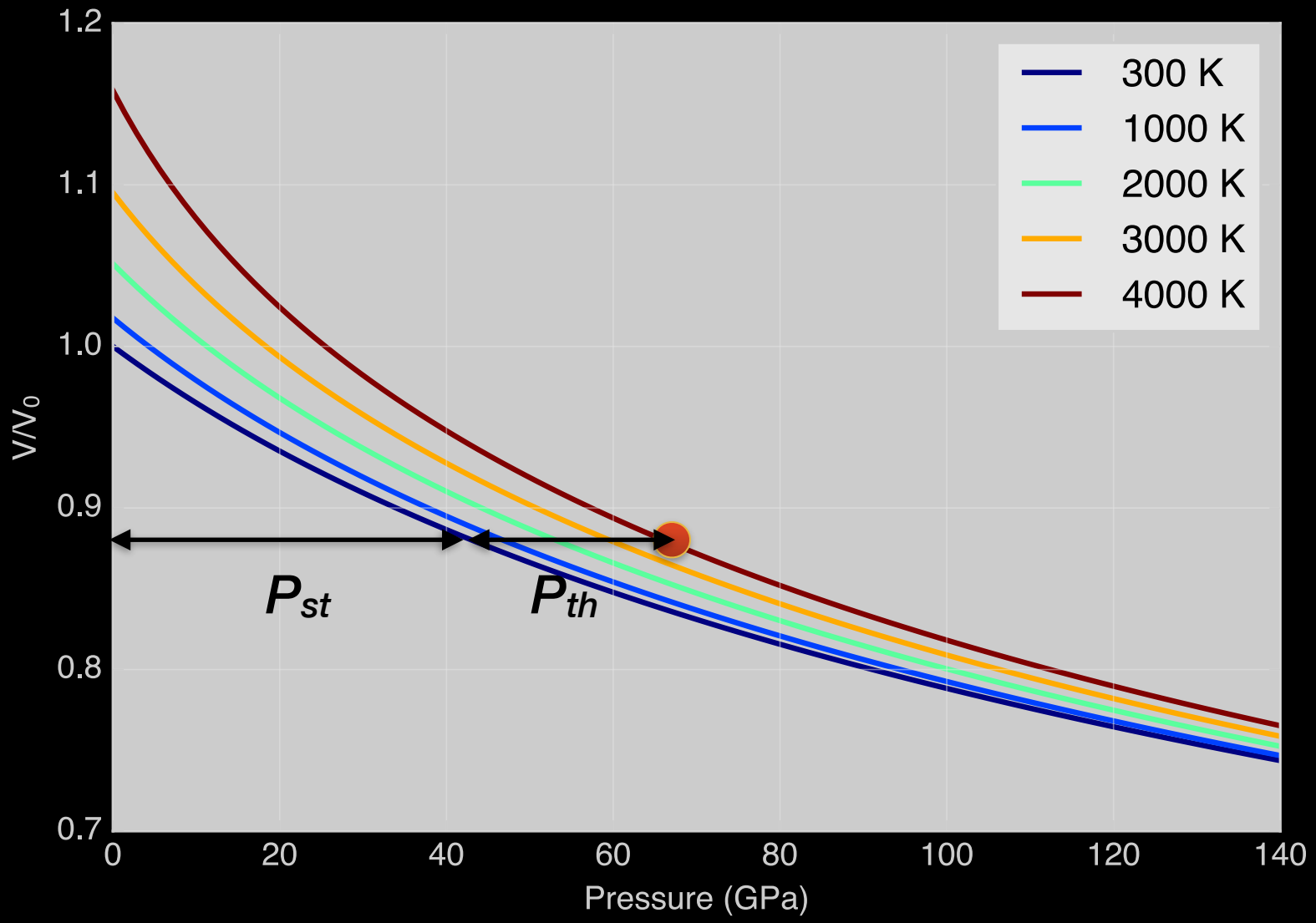
Do not mix equations and fitting results

Fei et al. (2007)



Shape of EOS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Pst
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Thermal expansion parameter

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P.$$

$$\alpha K_T(V,T) = \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial \Delta P_{th}}{\partial T}\right)_V$$

Thermodynamic Approach

$$\Delta P_{th} = P_{th}(V,T) - P_{th}(V,T_0) = \int_{T_0}^{T} [\alpha K_T]_V dT$$

Lattice Dynamic Approach

$$\Delta P_{th} = \frac{1}{V}\sum_i \gamma_i E_i \approx \frac{\gamma(V)}{V}\Delta E_{th}[\theta(V), T]$$

$$\gamma = \gamma_0 \left(\frac{V}{V_0}\right)^q$$

$$\theta = \theta_0 \exp\left(\frac{\gamma_0 - \gamma}{q}\right),$$ Debye temperature

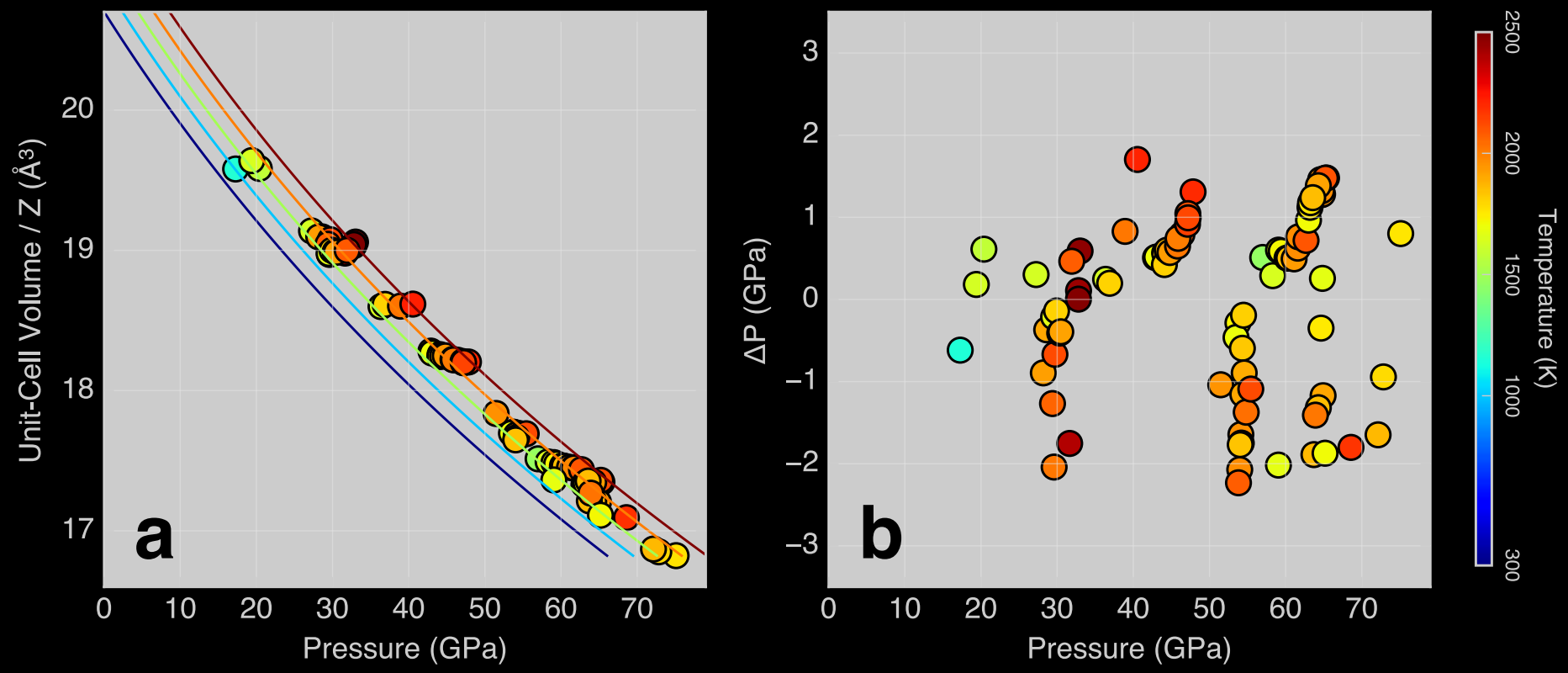
$$E_{th} = \frac{9nR}{x^3}\int_0^x \frac{\xi^3}{\exp\xi - 1}d\xi$$ Debye model

Parameters to Fit

$$V_0, K_0, K'_0$$

$$\gamma_0, q, \theta_0$$

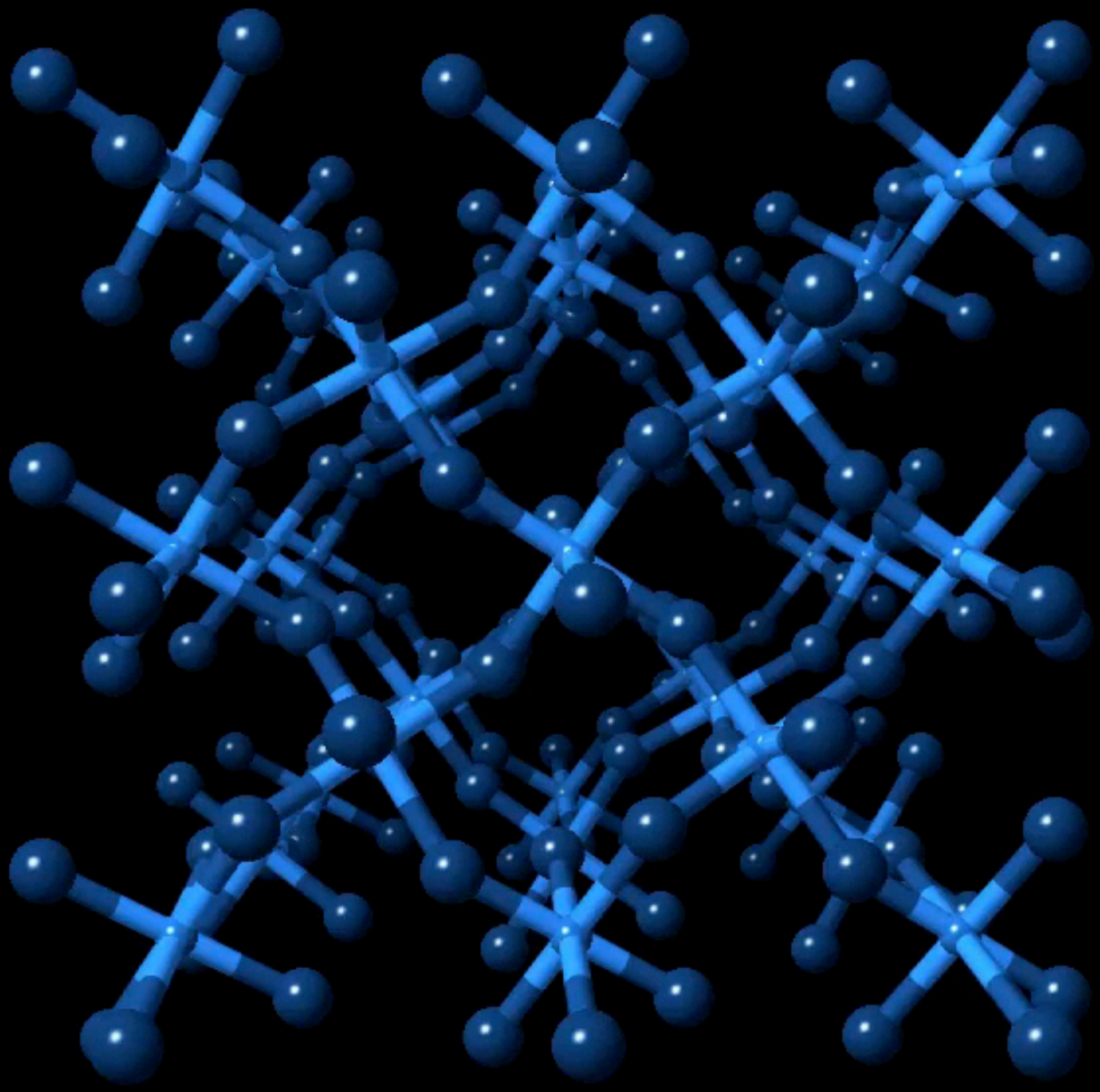
Example: *P-V-T* Fitting



SiC, Nisr et al., in prep.

Derivation of Thermodynamic Parameters

- Many useful parameters can be derived from Birch-Murnaghan-Debye and Vinet-Debye EOS.
- See Jackson and Rigden (1996, PEPI) for detail
- For example, K, α, $(\partial K/\partial T)_V$, $(\partial K/\partial T)_S$ at any given pressure and temperature



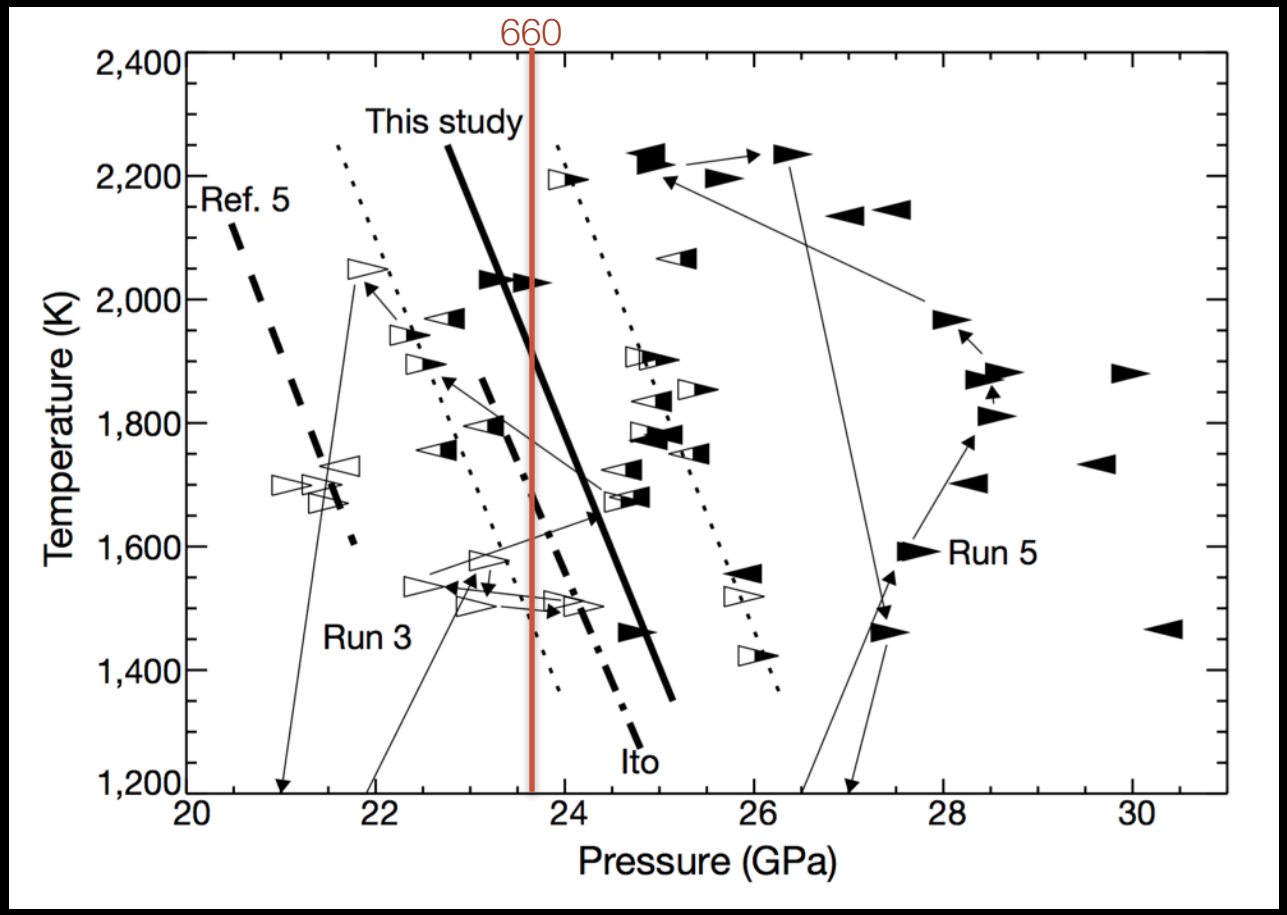
Lower Mantle Minerals

Fiquet et al (2000), Shim and Duffy (2000), Shim et al. (2000), Stixrude et al. (2011)

	K_0 (GPa)	γ_0	q	θ_0 (K)
Bridgmanite	250-260	1.3-1.7	1.2-1.7	1000
Ferropericlase	160-165	1.4	1.3	673
$CaSiO_3$ Pv	220-250	2	0.6	1000

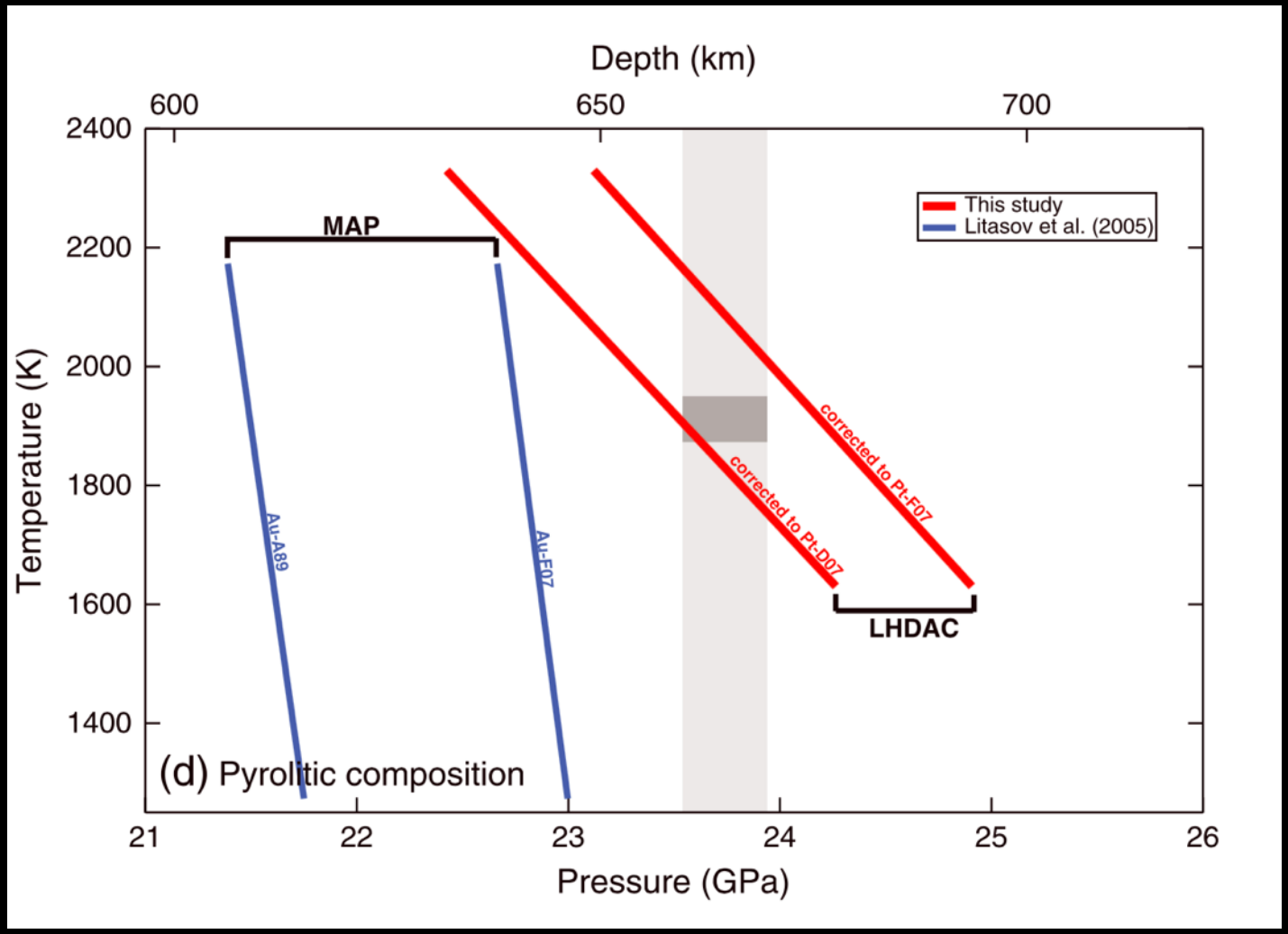
- Density and elasticity of pyrolite agree reasonably well with those of PREM.
- Density of MORB is 2-3% higher than pyrolite throughout the lower mantle.

Pressure Scale



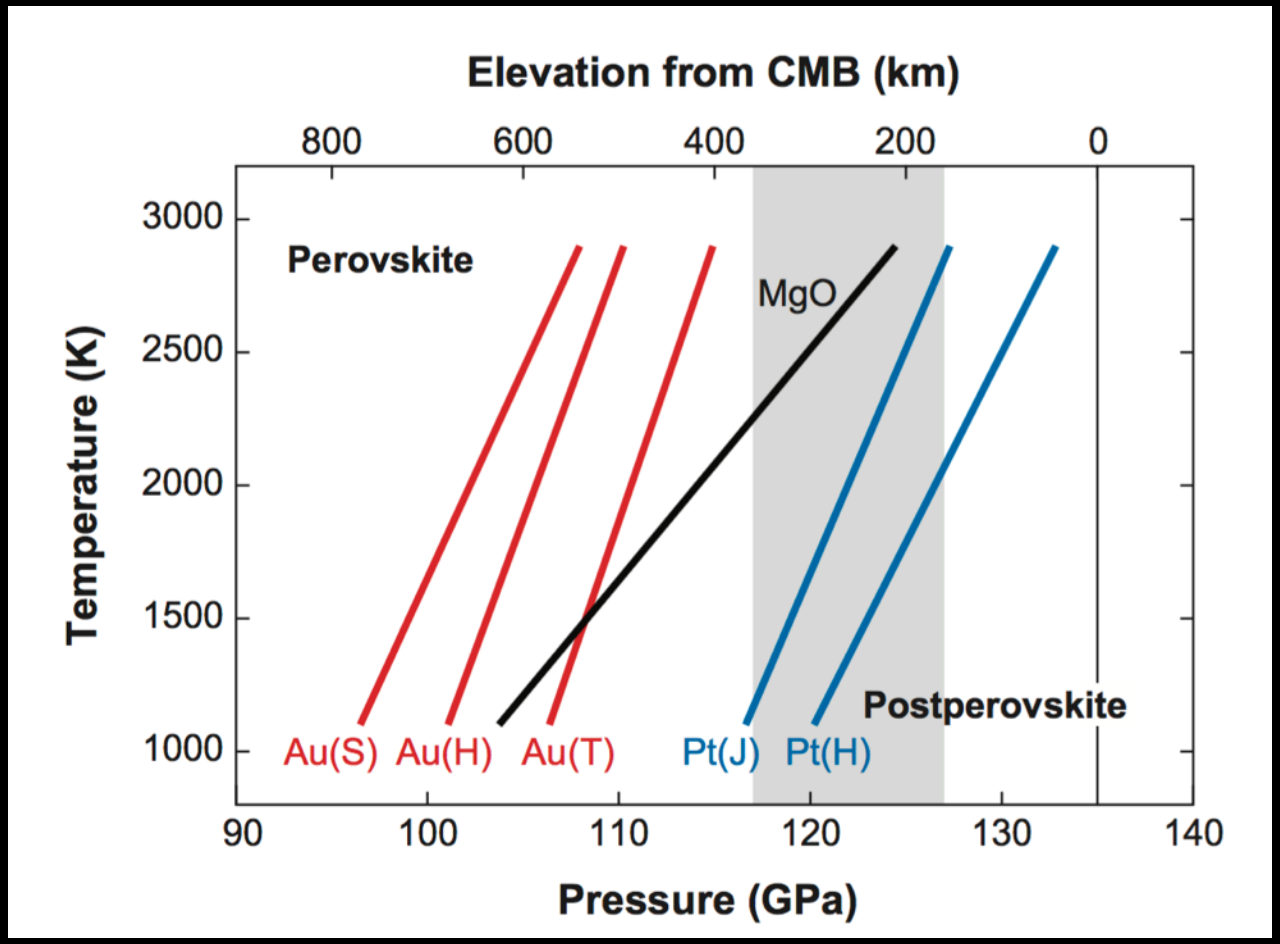
Shim et al. 2001

Pressure Scale: Post-Spinel



Ye et al. 2014

Pressure Scale: Post-Perovskite

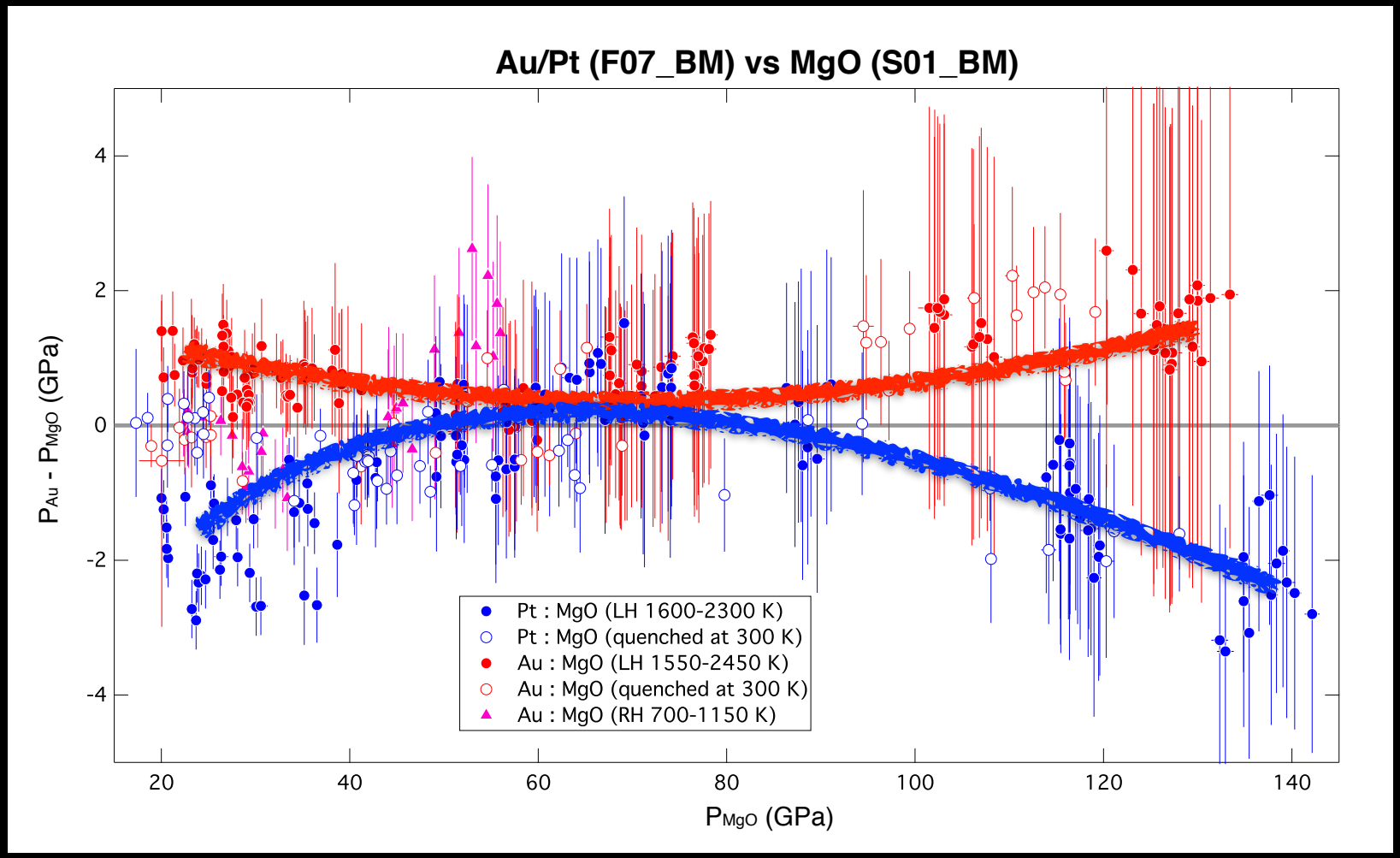


Shim 2008

So What is Problem?

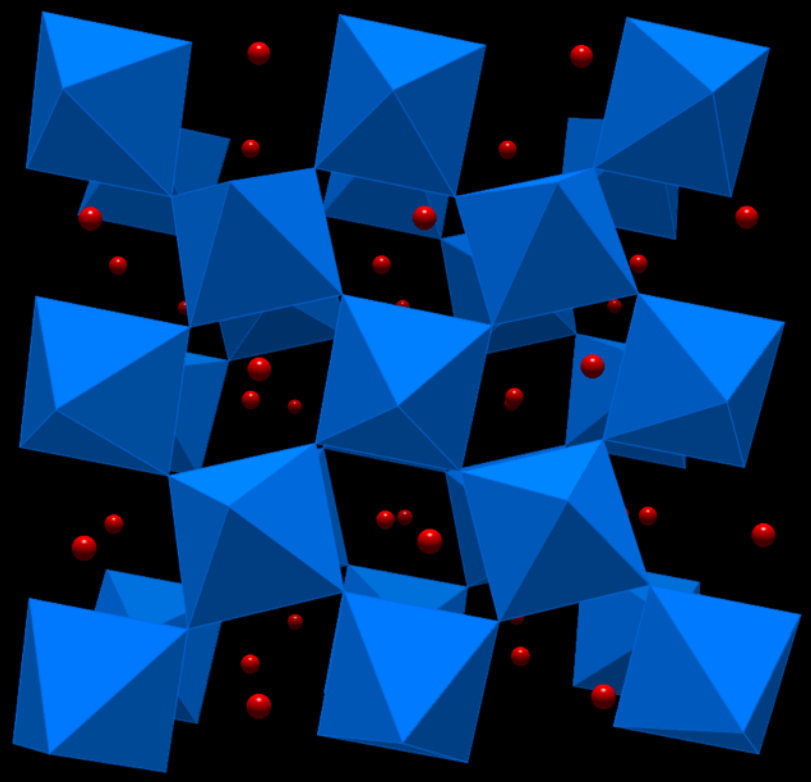
- Stress conditions
- Temperature conditions
- Extreme thermal contribution — electronic contribution in metal pressure standards

P(Au) — P(Pt) — P(MgO)



Ye et al. (2016) in prep.

Bridgmanite



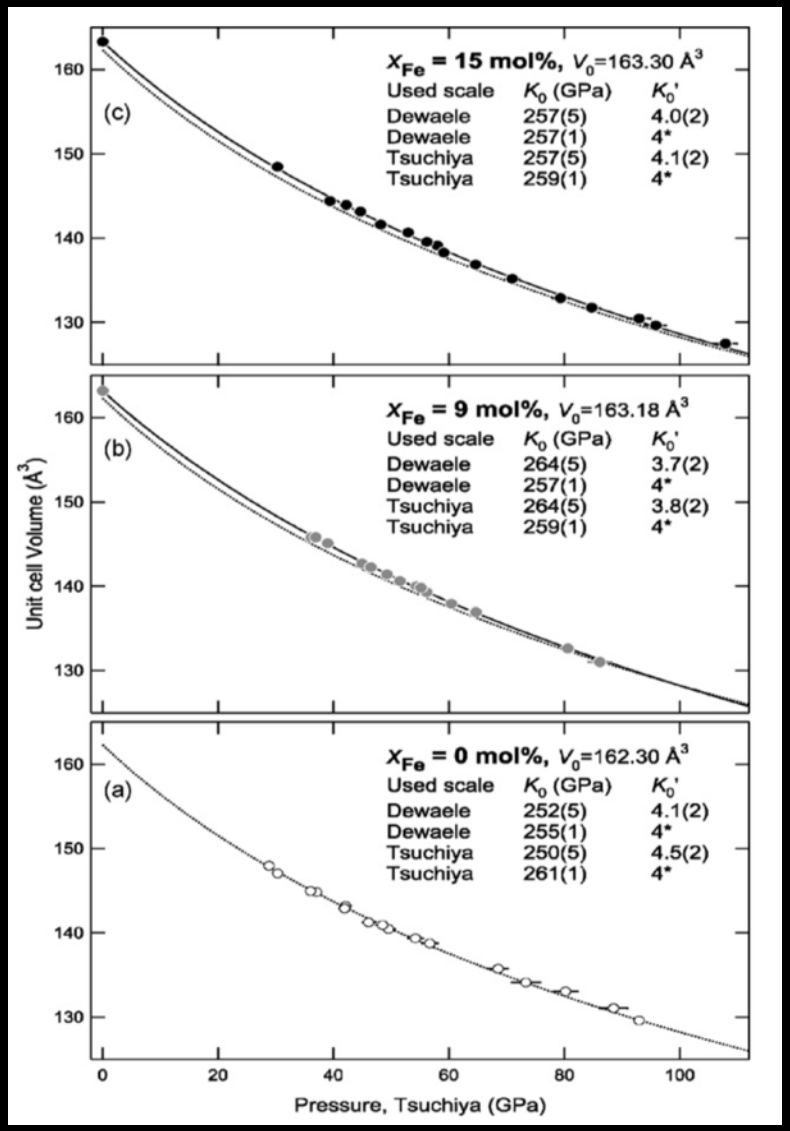
$^{VIII}Mg^{2+}{}^{VI}Si^{4+}O_3$

Fe^{2+}

Fe^{3+}

Al^{3+}

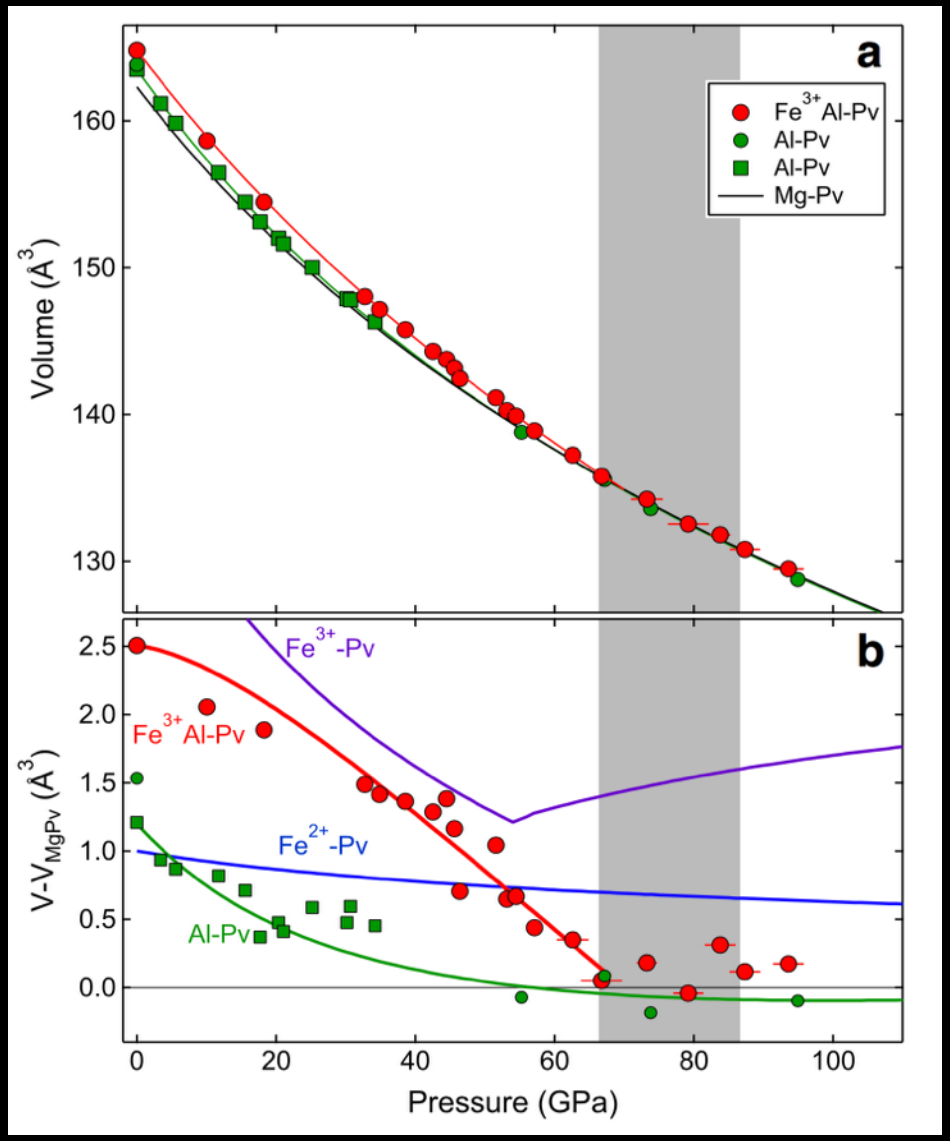
Bridgmanite



Fe^{2+}

Lundin et al. 2008

Bridgmanite

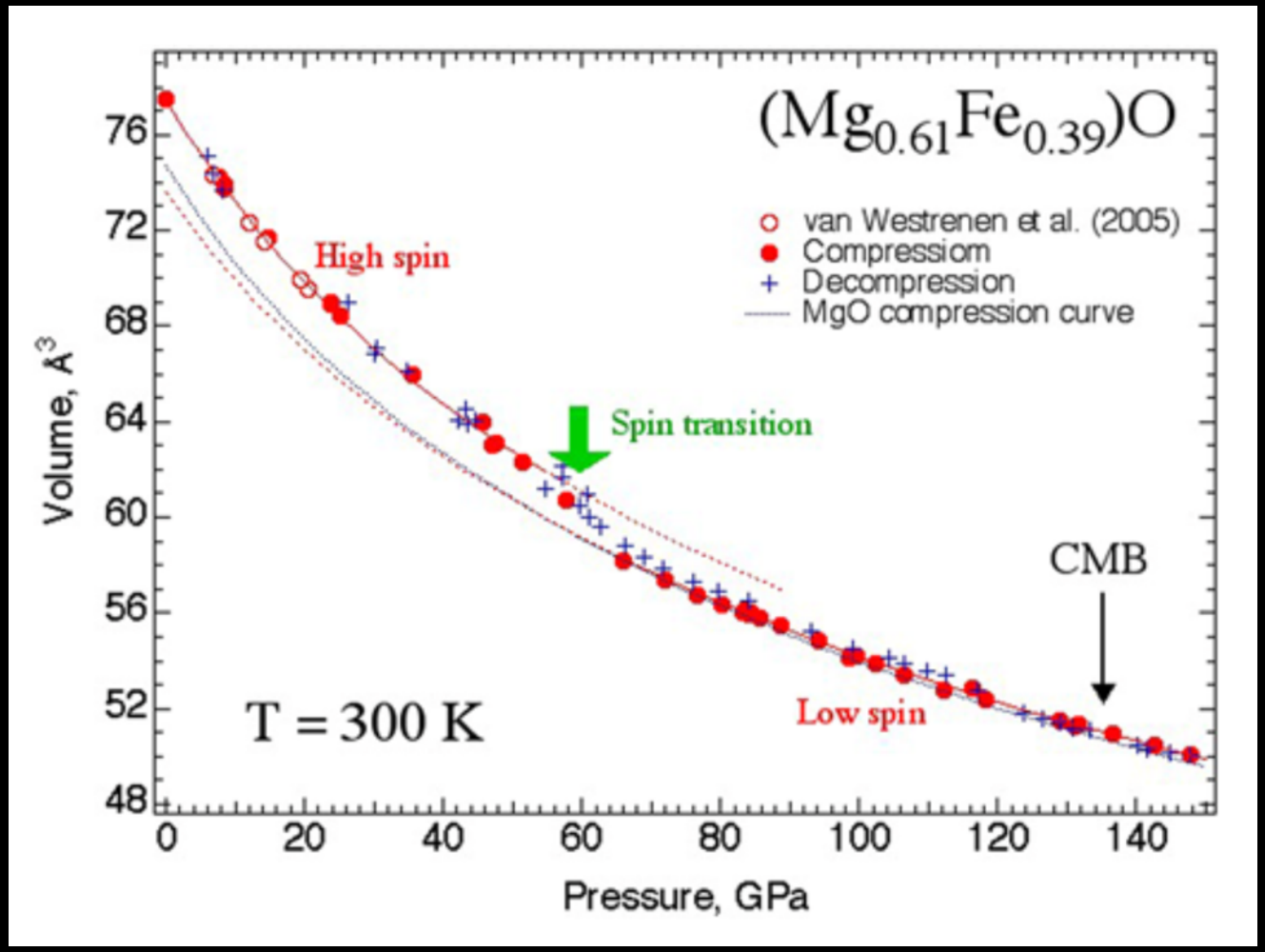


Fe^{3+}

Al^{3+}

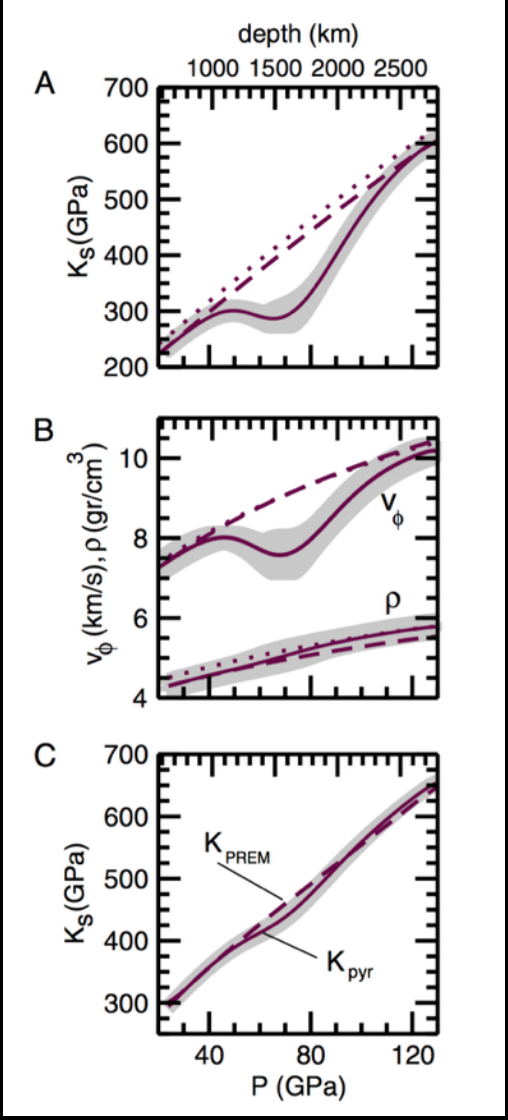
Catalli et al. 2011

Ferropericlase



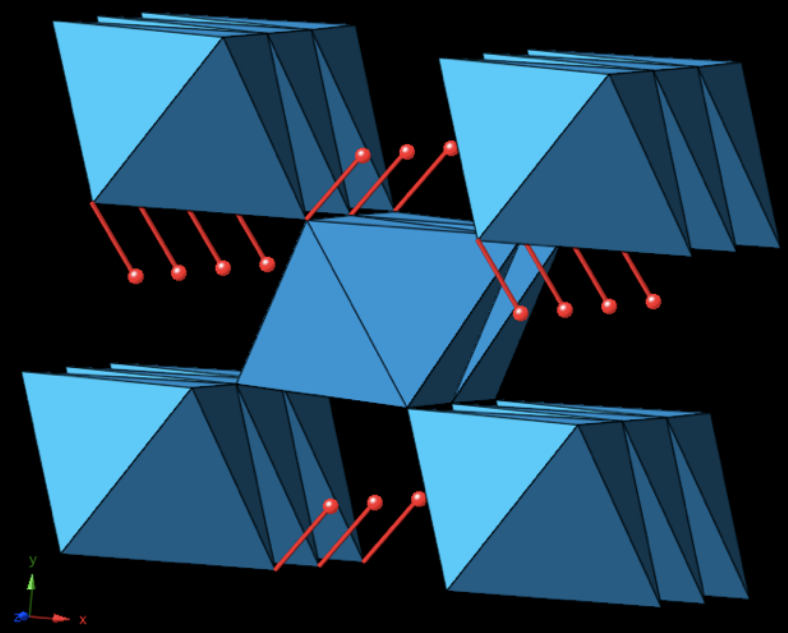
Fei et al. 2007

Ferropericlase



Wentzcovitch (2009)

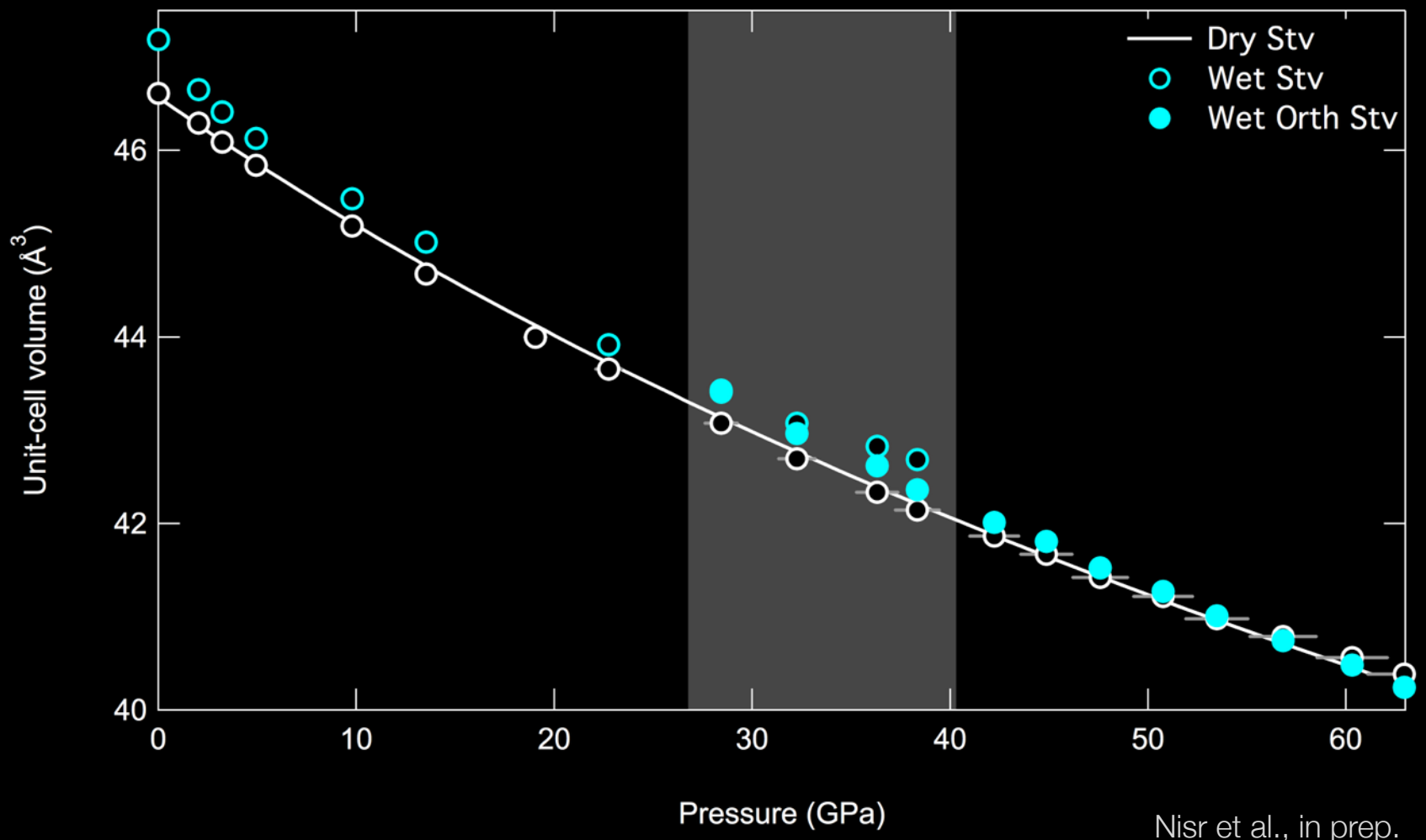
Stishovite: Effect of Water



- δ—AlOOH
- Phase H (Nishi et al. 2014)
- δ—H (Ohtani et al. 2014)
- SiO_2 (Spektor et al. 2011)

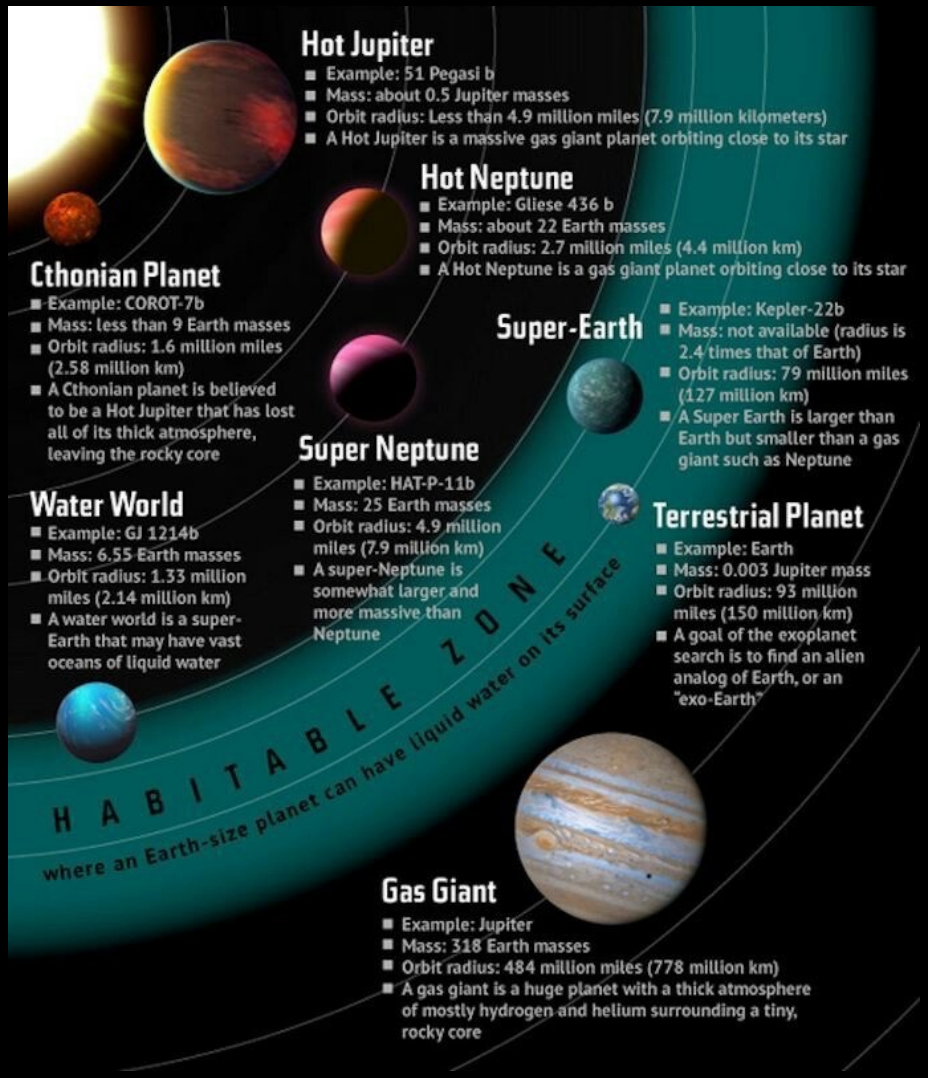
$$\Delta G = \Delta U + P\Delta V - T\Delta S$$

Stishovite: Effect of Water



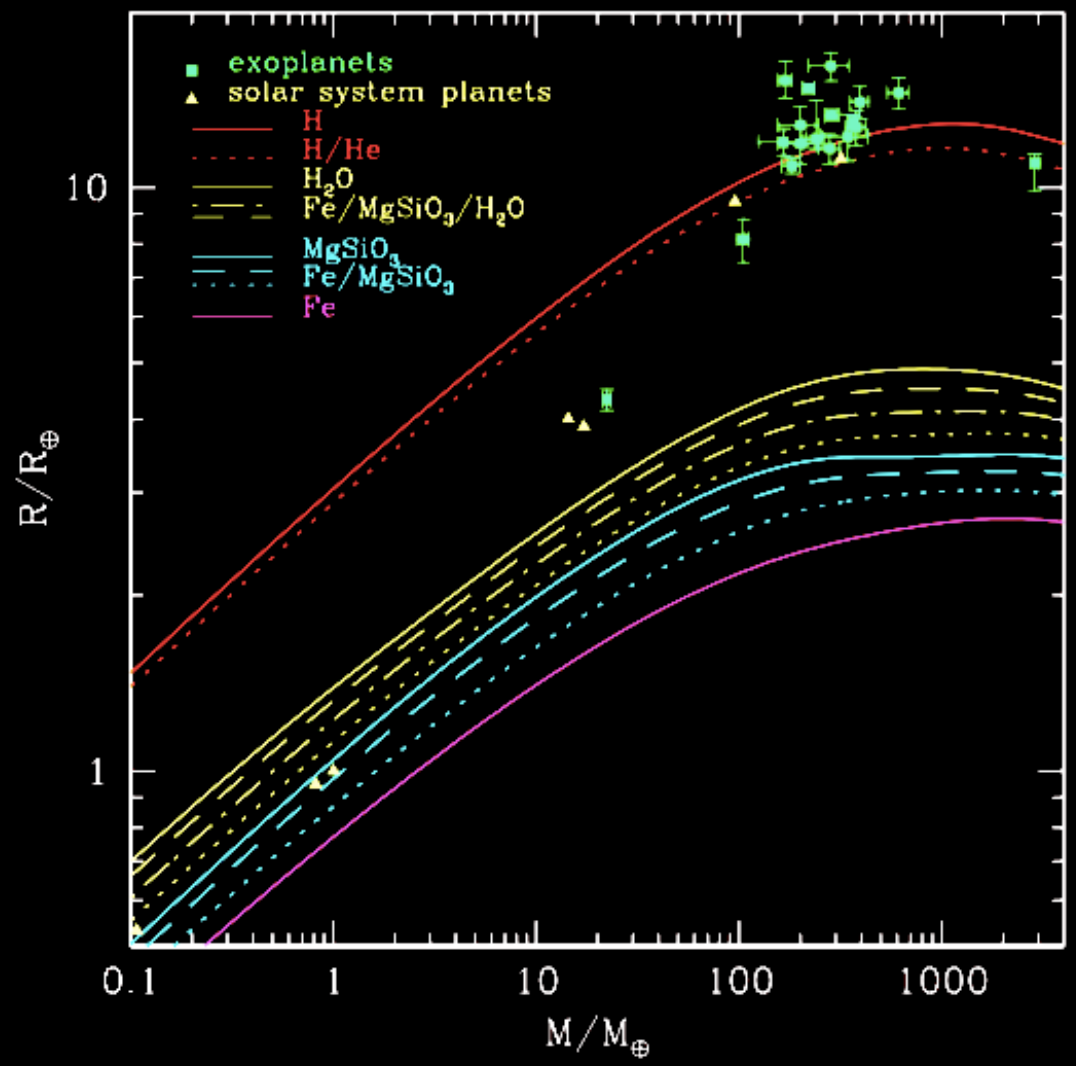
Nisr et al., in prep.

Nexus for Exoplanet System Science



http://www.nexss.io

Mass-Radius Relations

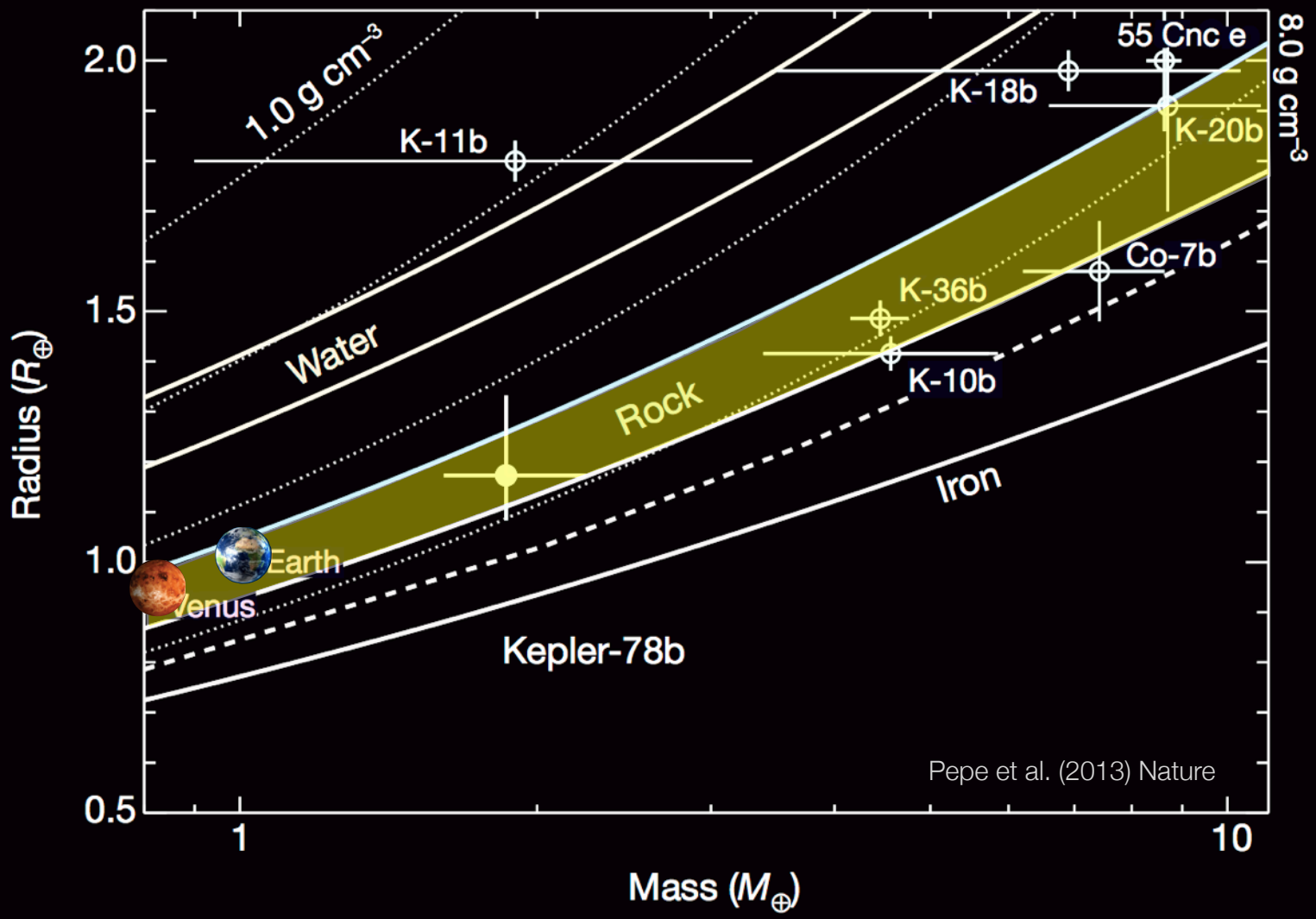


Hydrogen

Water
Silicate
Iron

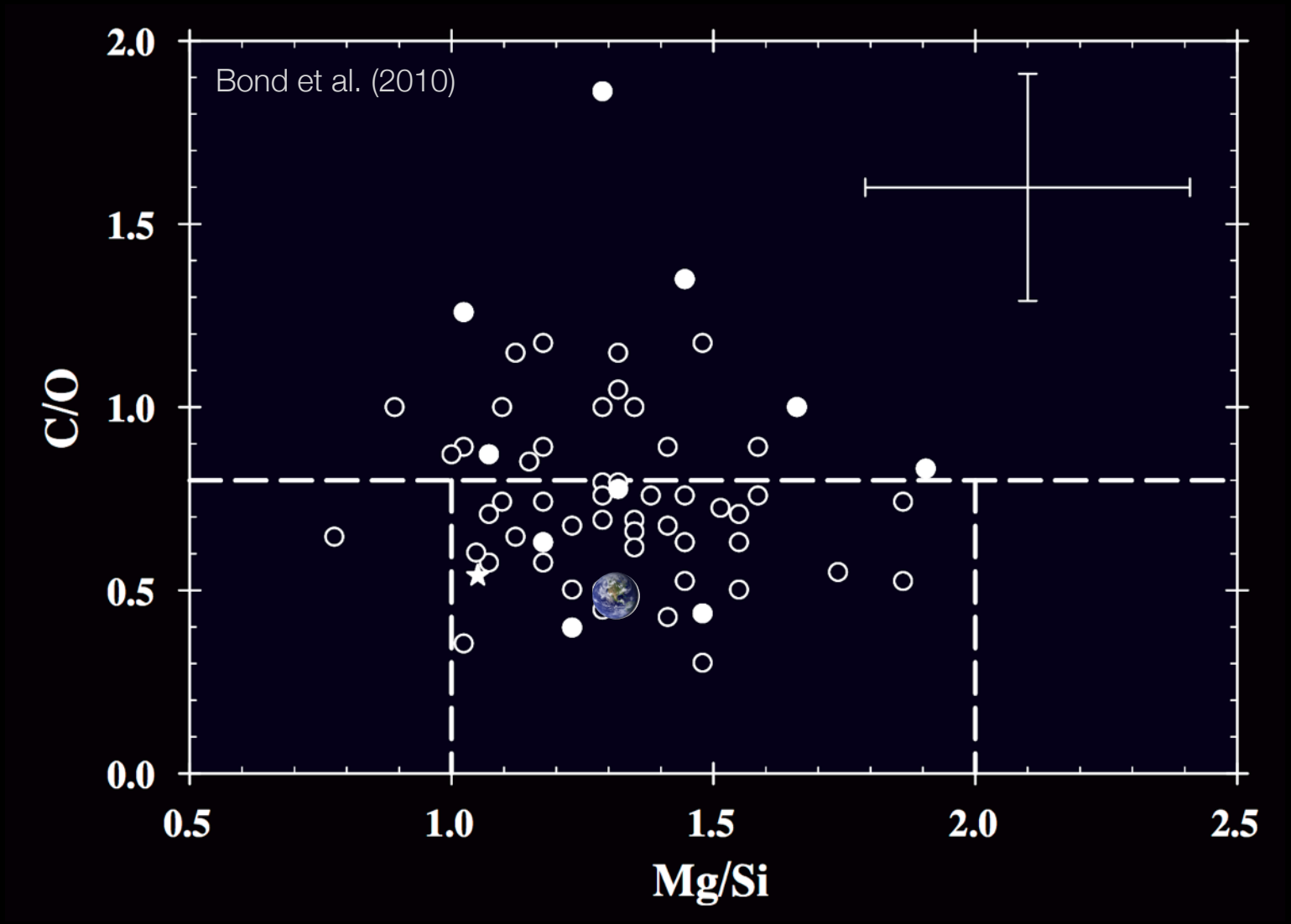
Seager (2007)

Earth-Like Exoplanets

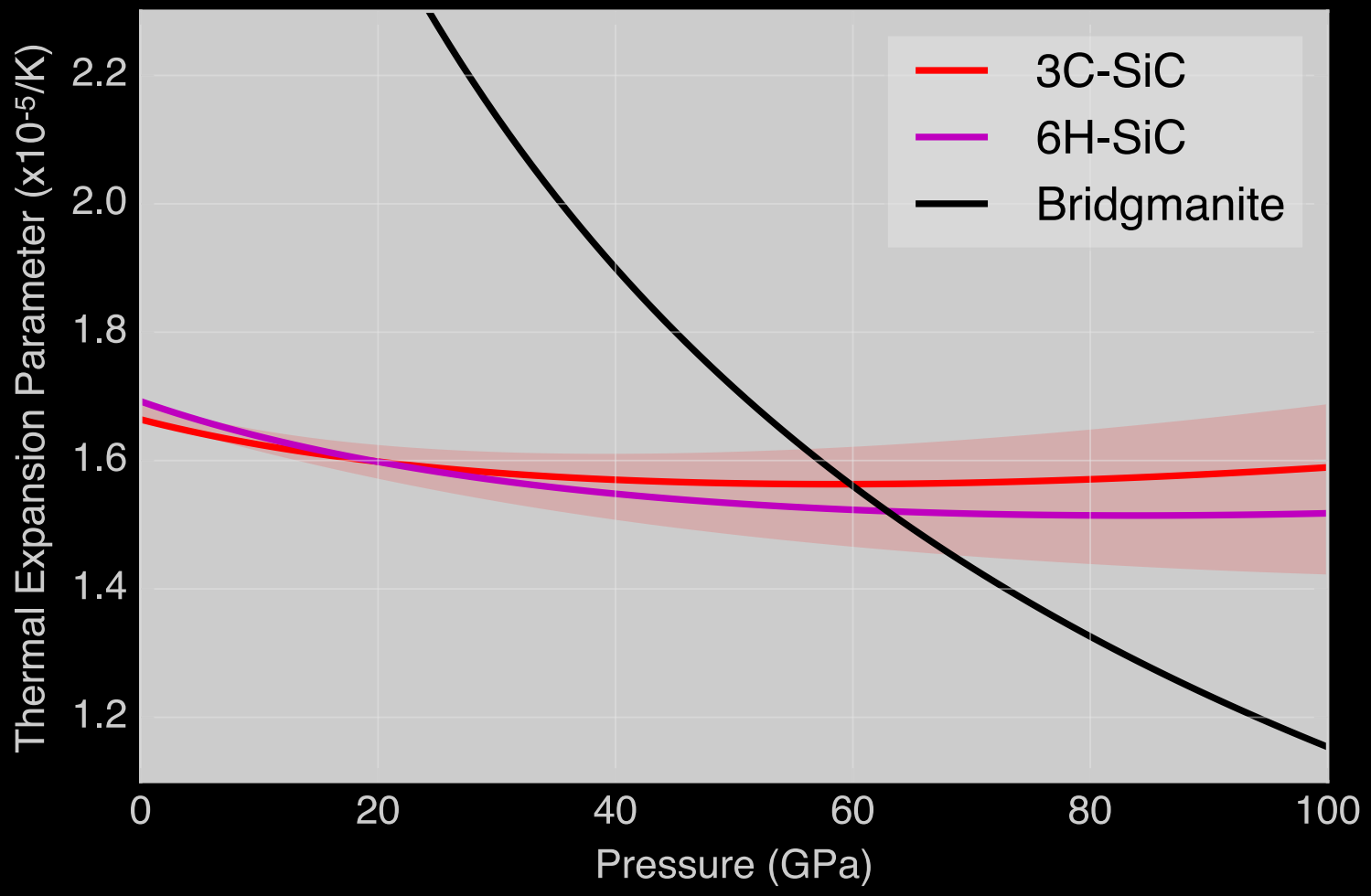


Pepe et al. (2013) Nature

Elemental Abundances



Carbide Planets



Nisr et al., in prep.

Further Readings

- Jackson and Rigden (1996) PEPI
- Anderson (2000) GJI
- Shim and Duffy (2000) AmMin

Future

- Better description of thermal part
- Better description of electronic contribution
- New experimental techniques
- Demand from exoplanet field
- Database with community agreement (?)