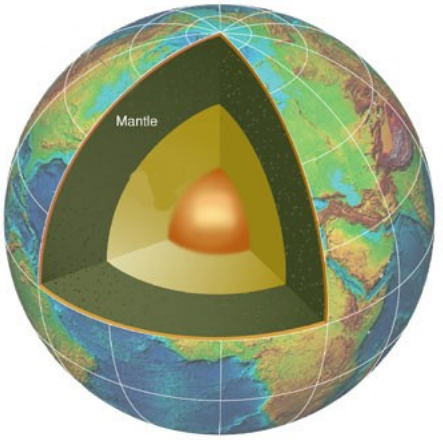
Institute of Nuclear Physics, Cracow, Poland

Deep Earth thermodynamics from phonons

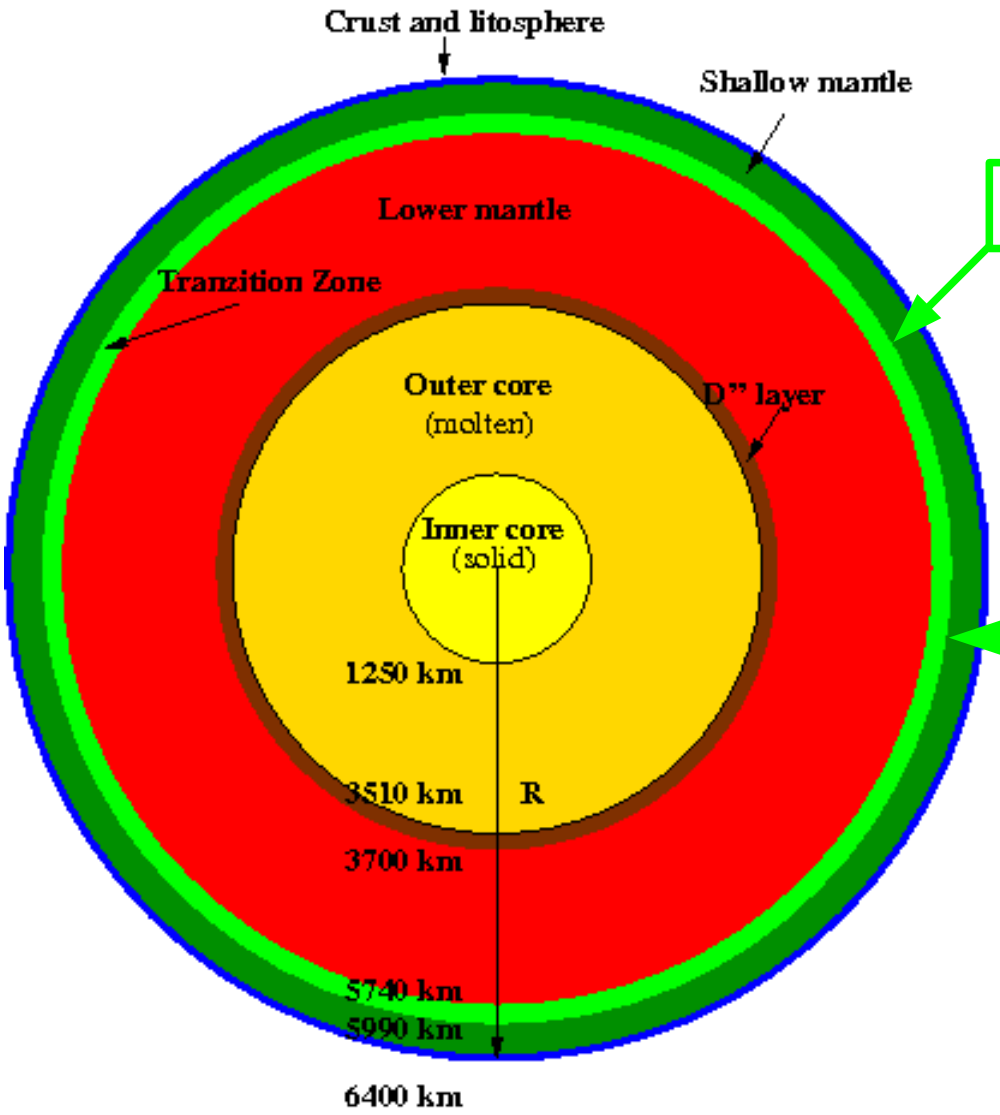


Kamil Tokár

Department of Material Research by Computers

Kraków, Poland 1-4th DEC 2010

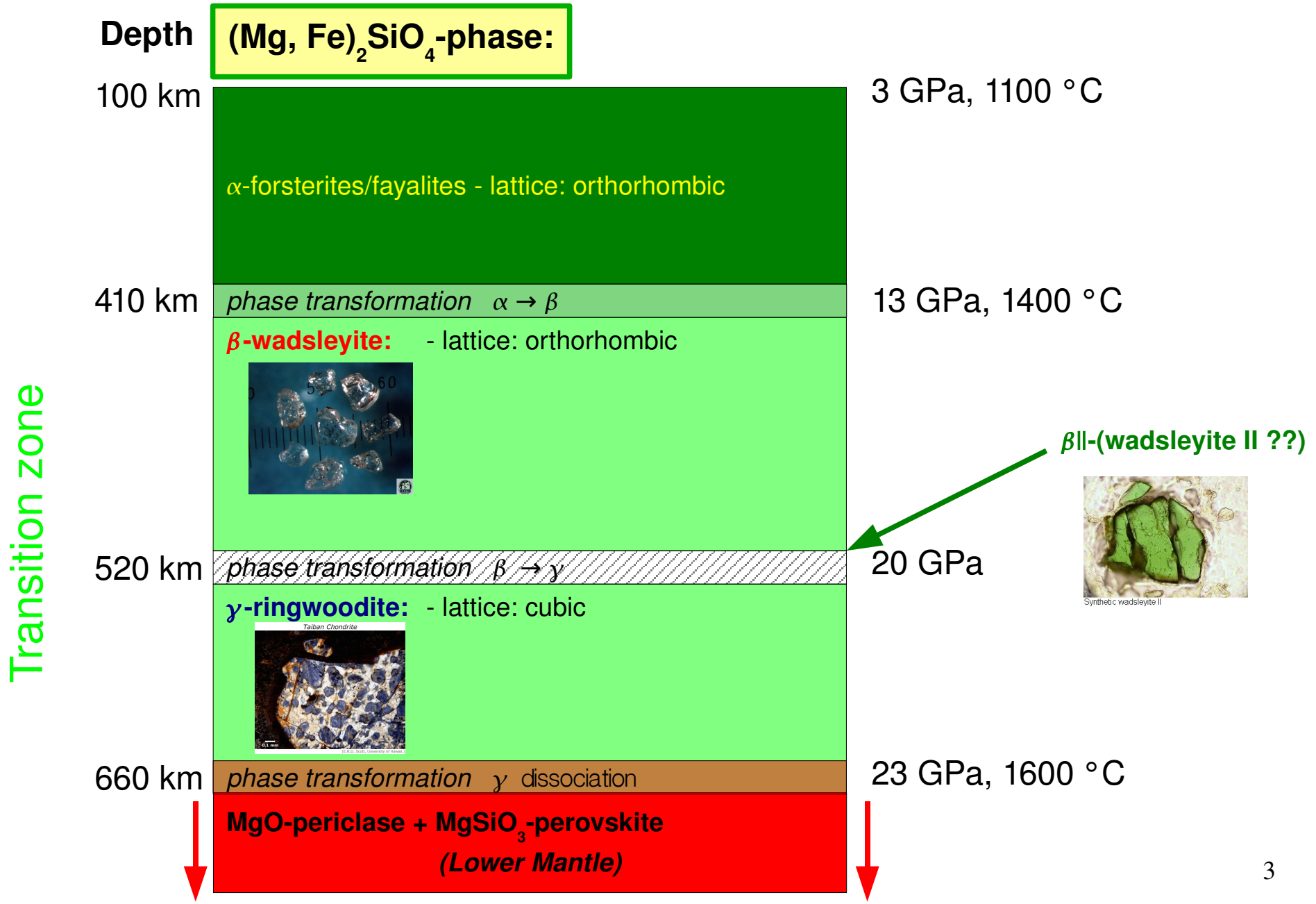
Structure of Earth interior - overview



Zone of interest

	depth
Continental crust:	0-75 km
Oceanic crust:	0-10 km
Upper mantle:	10-400 km
Transition zone:	400-650 km
Lower mantle:	650-2 890 km
D" layer:	2 700-2 890 km
Outer core:	2 890-5 150 km
Inner core:	5 150-6 370 km

Structure of Earth's Transition Zone – simplified description



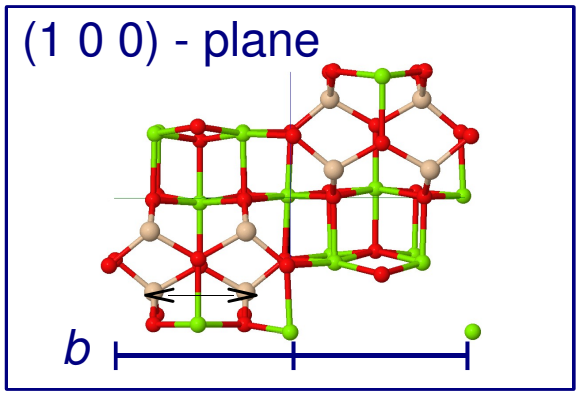
Wadsleyite against Wadsleyite II

Wadsleyite II – Mg_2SiO_4 is a recently detected magnesium-iron silicate phase - a potential host for hydrogen in the Transition Zone, between the wadsleyite and ringwoodite zones (*Smyth J.R. and Kawamoto T. (1997)*).

Differences

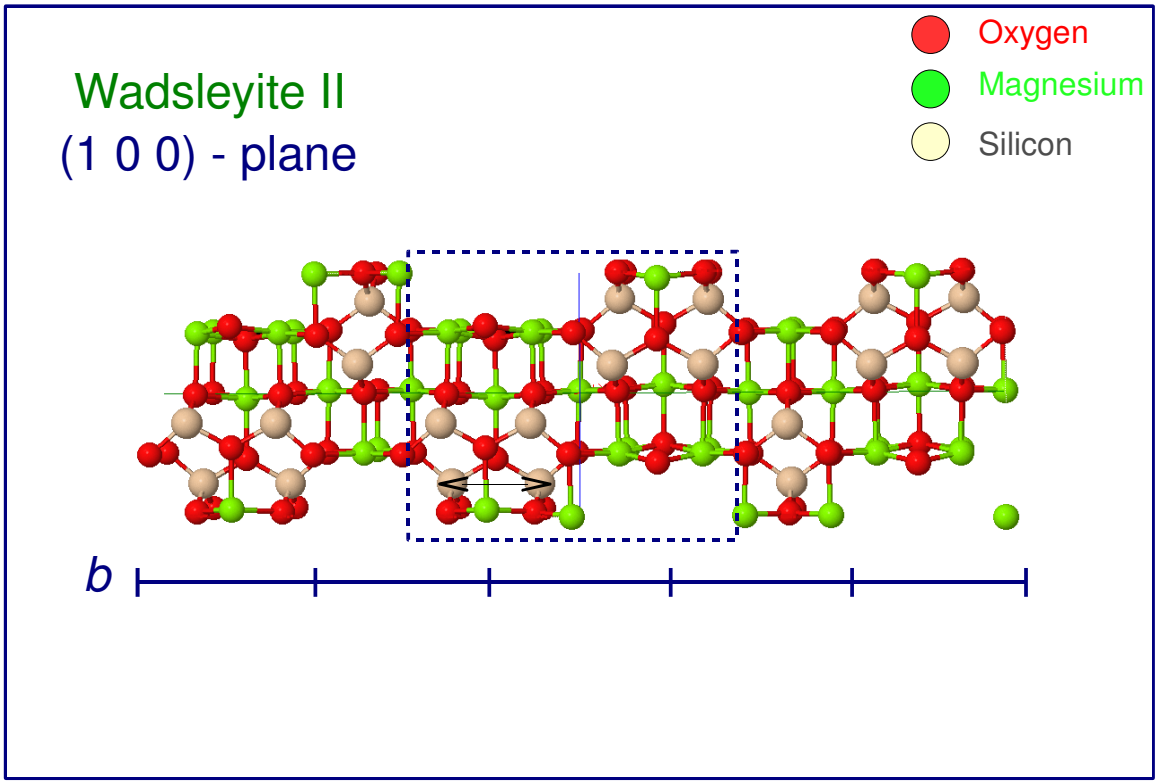
Space symmetry: I*mma*

a=5.698 *b*=11.462 *c*=8.257 [Å]



Wadsleyite

a=5.749 *b*=28.791 *c*=8.289 [Å]

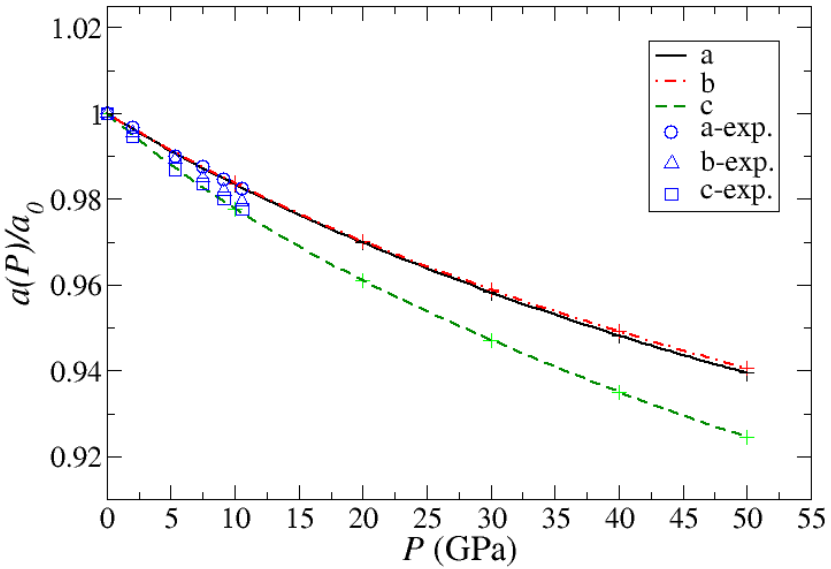


Methods used in theoretical study of Wadsleyite II

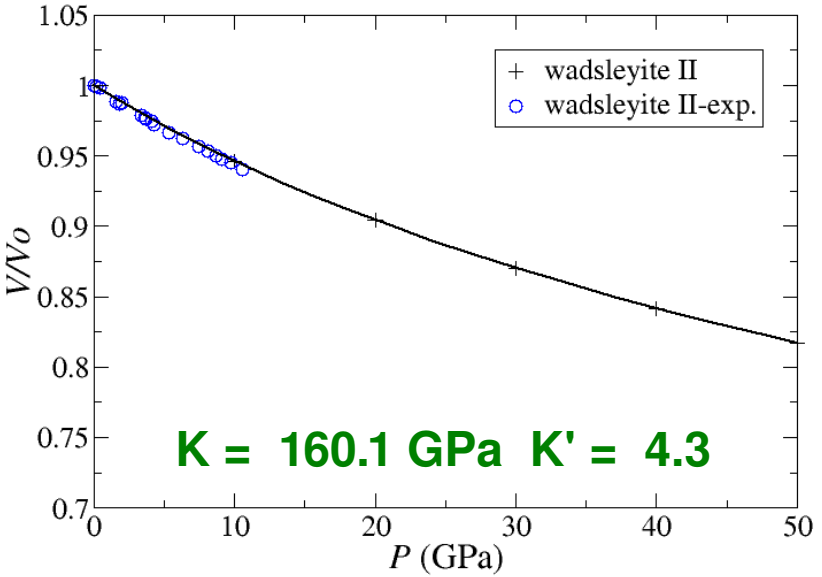
- DFT+GGA with PBE functional and PAW approach
- Direct method for determination of the lattice dynamics
- Quasi-harmonic Approximation (QHA) in Thermodynamic model

Unit cell parameters of Wadsleyite II – pressure dependence

Lattice parameters



3rd – order Birch-Murnaghan EOS



Comparison of lattice constants

Wadsl. II	*a* [Å]	*b* [Å]	*c* [Å]
10.56 GPa [a)]	**5.583**	**28.426**	**8.056**
10.00 GPa [b)]	**5.654**	**28.322**	**8.105**
0.00 GPa [b)]	**5.749**	**28.791**	**8.289**

Comparison of bulk moduli

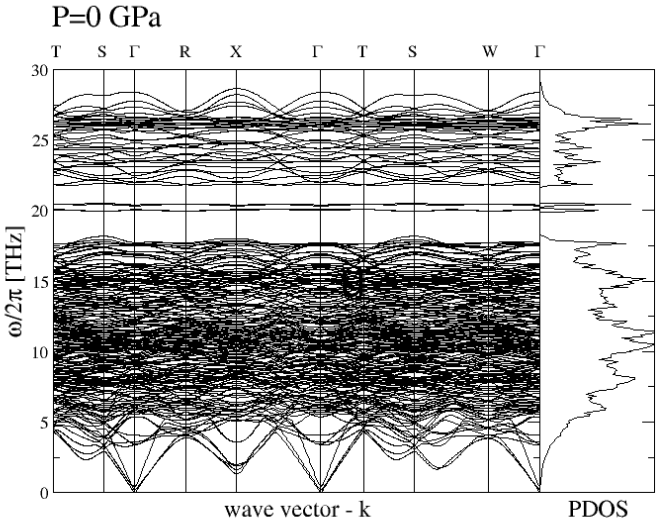
(Smyth et al. (2005))

Wadsl. II	H_2O wt%	K (GPa)	K'
anhydrous [a)]	-	**167±10**	-
hydrous [a)]	**2.1**	**151±6**	**6±2.5**
	2.8	**145.6±2.8**	**6.1±0.7**
this study [b)]	-	**160.1**	**4.3**

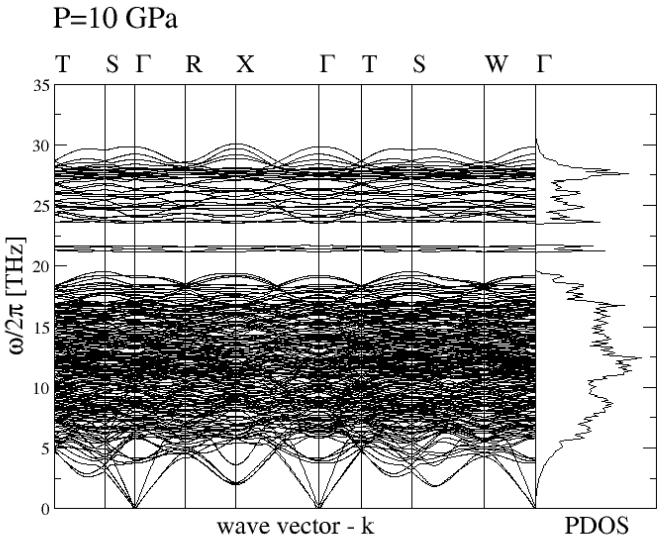
[a)] exper. *Smyth et al.,Phys.Chem.Mineral **31**,691 (2005)*

[b)] *calc. Tokár et al.,J.Phys.: Condens. Matter **22**,145402 (2010)*

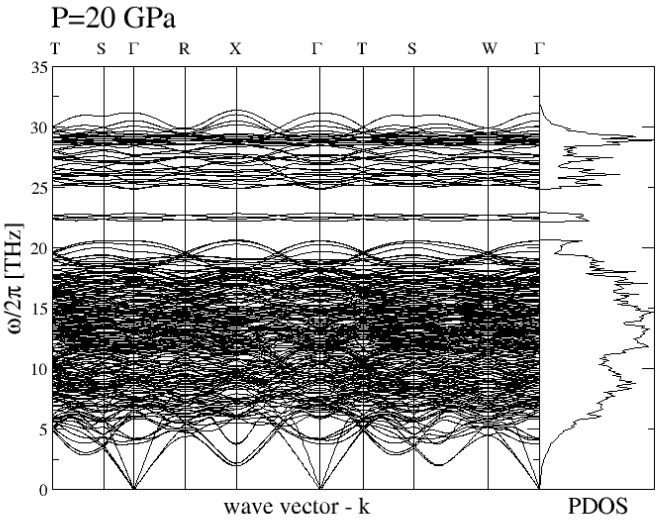
Lattice stability of the Wadsleyite II at high pressure (calculation)



External pressure: P=(0-20 GPa)
210 phonon vibration modes



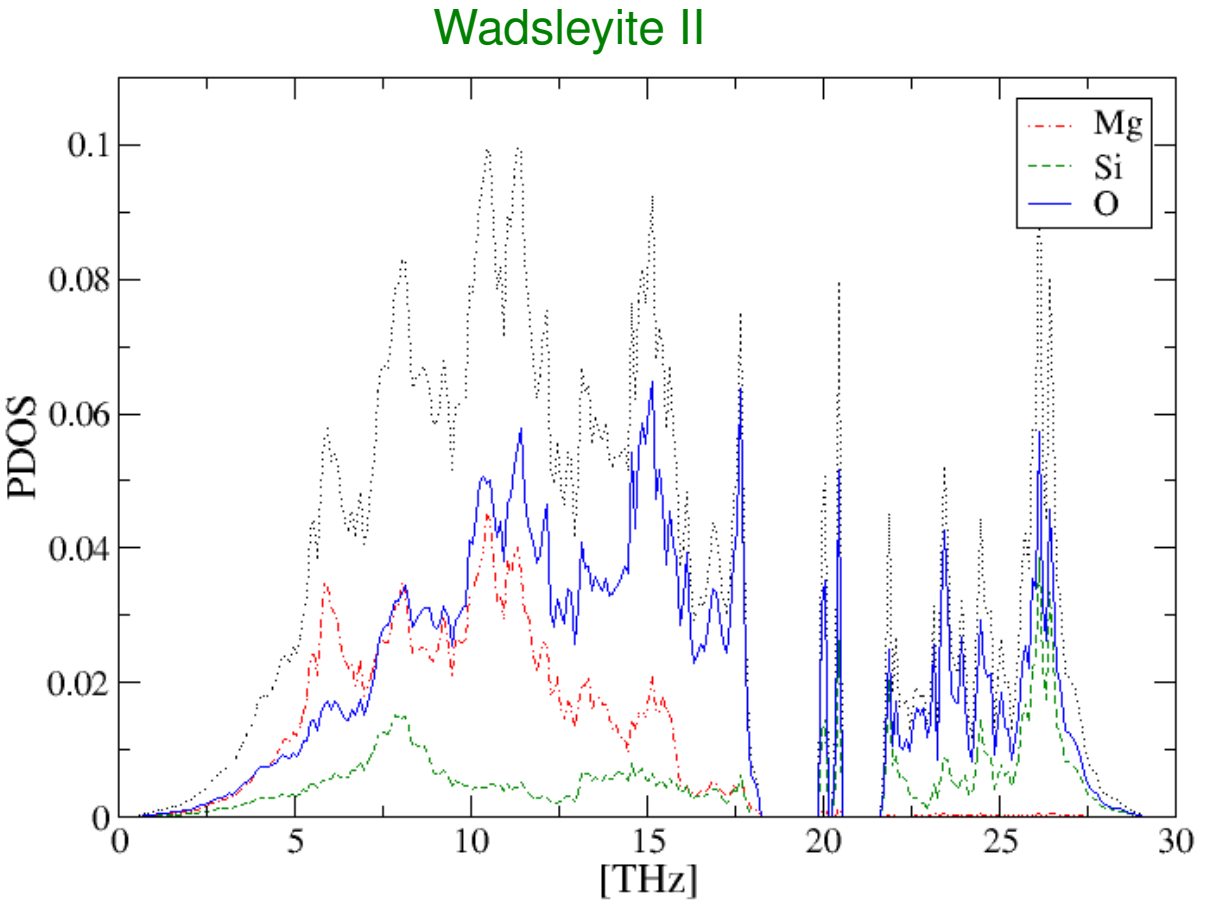
Synthesis at ~17.5-18.5 GPa



Phonon dispersion curves: **No soft phonon behavior**

Conclusion:
Crystal of wadsleyite II has **mechanically stable structure**

Lattice dynamics: Partial Phonon DOS of Wadsleyite II: p=0 GPa



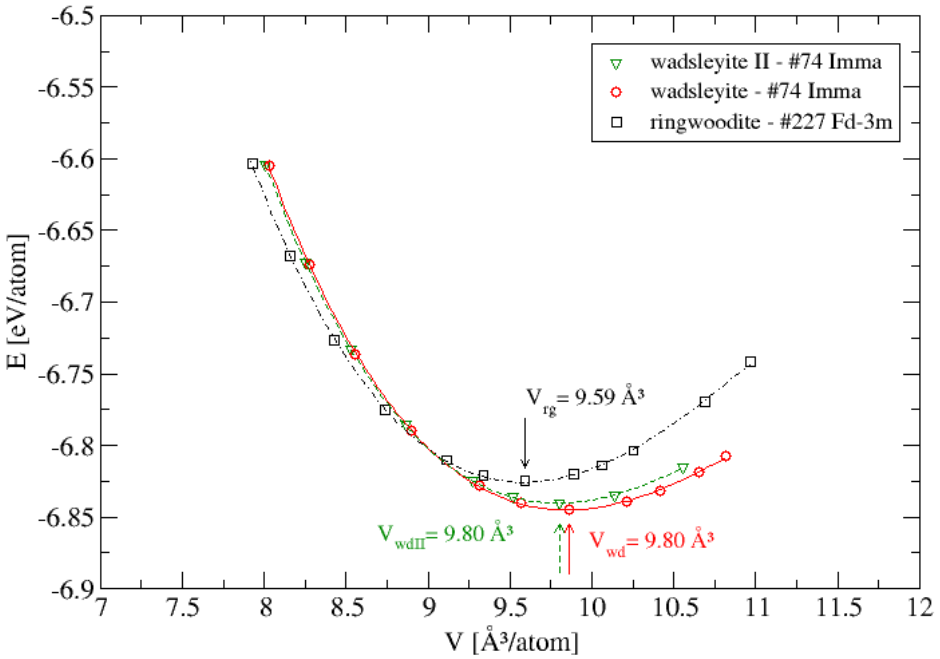
Constraining of the complete pT diagram

Construction of thermodynamical model:

- **Lattice dynamics** calculated from *ab initio*
- **PDOS** of all considered Mg_2SiO_4 phases: wadsleyite, ringwoodite, wadsleyite II + (periclase+perovskite)
- **QHA** approximation to parametrize thermodynamical functions of the phases and constrain coexistence boundaries

QHA approximation used to derive pT diagram

DFT+GGA :: Static energy $E_{stat}(V)$



Lattice dynamics:

PDOS $g(\omega)$ ==> $F_{phon}(T, V)$

$$F_{phon}(T,V) = k_B T \int_0^\infty g(\omega) ln\left(2sh\frac{\hbar\omega}{2k_B T}\right) d\omega$$

Free energy:

$G_{phas}(T, p)=E_{stat}(V) + F_{phon}(T, V) + pV$

Effective chemical potential:

$\mu_{phas}(T, p) = G_{phas}(T, p) /N$ :: *p=const.*

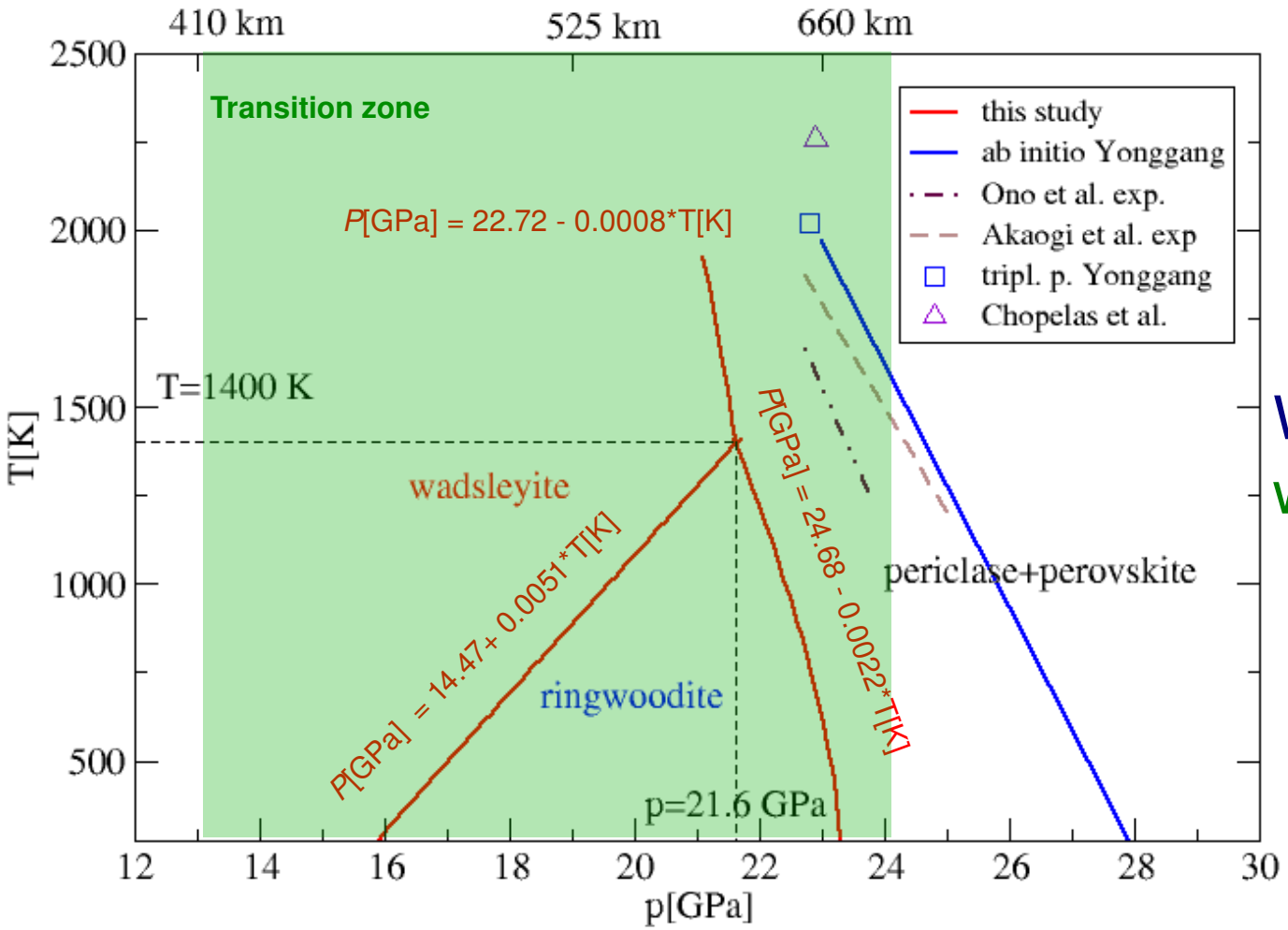
N – number of particles in the unit cell

Phase boundary:

Locus of points {*p,T*} with condition:

$\mu_\beta(T, p)=\mu_\gamma(T, p)$ ===> {*p, T*}

Complete Mg_2SiO_4 phase diagram and triple point at high pressure



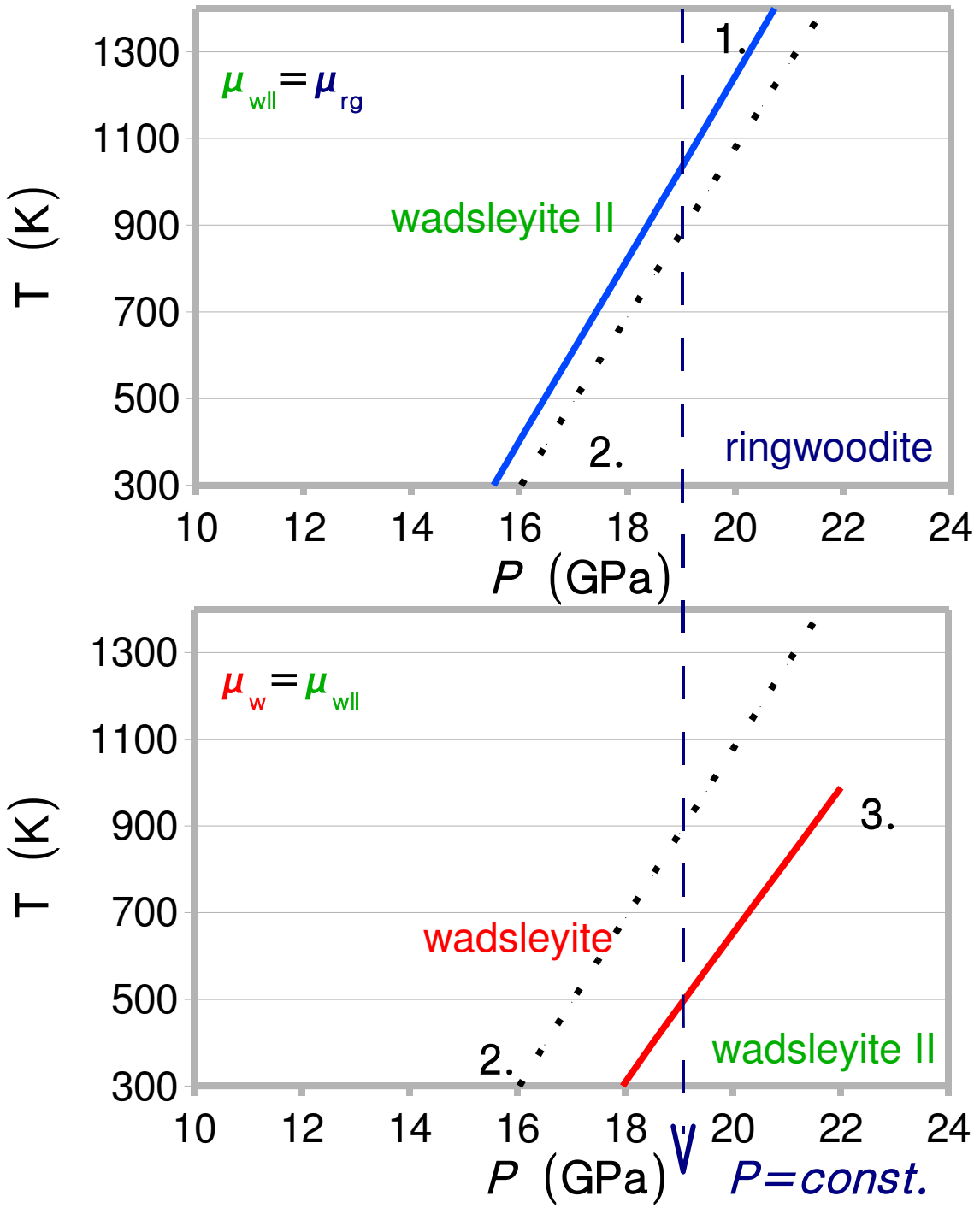
Cs=dp/dt

Where is wadsleyite II ??

Triple point: phases meet at p**=21.6 GPa, T=1400 K**

Dissociation: (β ; γ) - Mg_2SiO_4 ---> { MgO(periclase) + $MgSiO_3$(perovskite) }

Wadsleyite II phase relations to wadsleyite and ringwoodite (estimation)



Phase boundaries from QHA

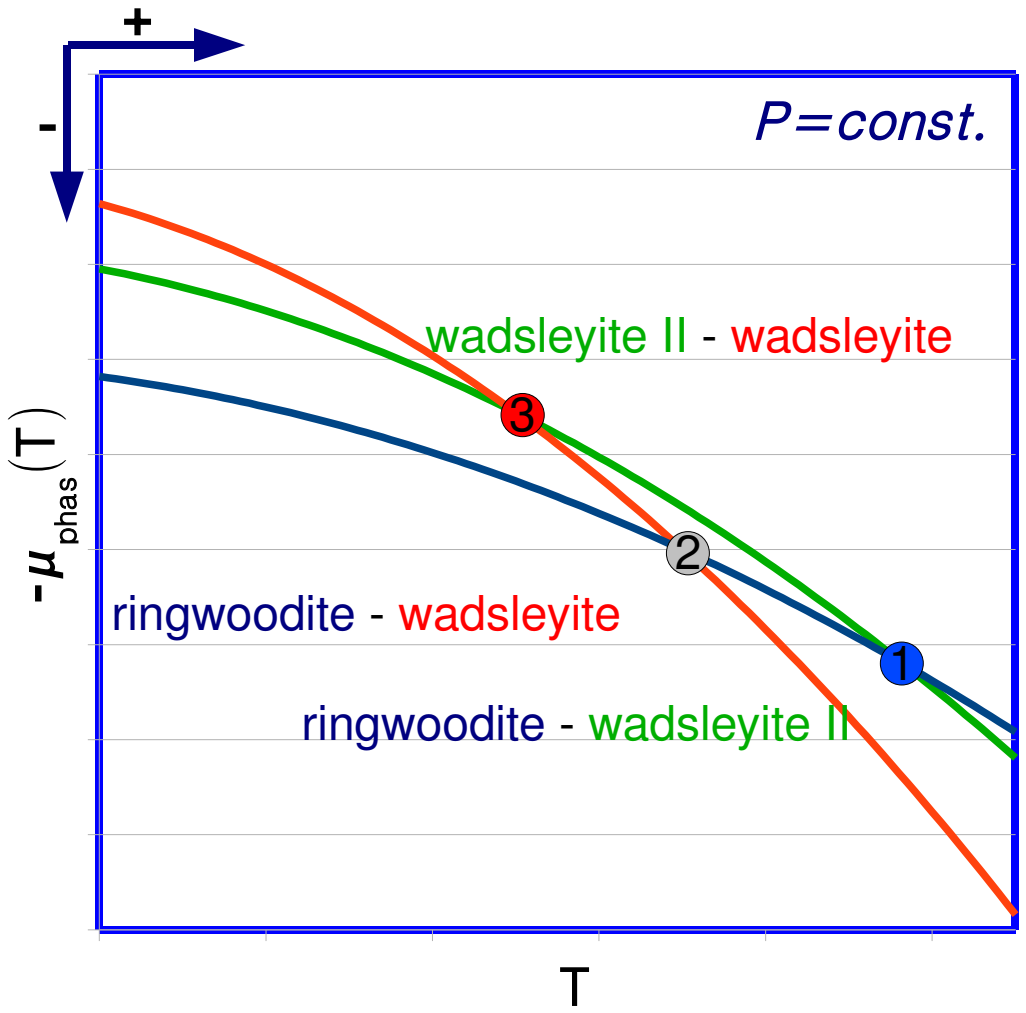
Clapeyron slopes:

1. ——— wadsleyite II-ringwoodite:
   P [GPa] = 14.13+ 0.0047*T[K]

2. ▪ ▪ ▪ wadsleyite-ringwoodite:
   P[GPa] = 14.47+ 0.0051*T[K]

3. ——— wadsleyite-wadsleyite II:
   P [GPa] = 16.21+ 0.0058*T[K]

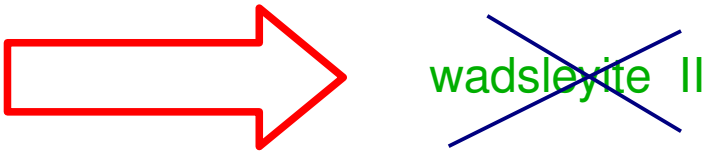
Wadsleyite II phase thermodynamic stability in Mg_2SiO_4 system



Thermodynamic relations:

$$(\mu_{wd} < \mu_{wdII}) \text{ OR } (\mu_{rg} < \mu_{wdII})$$

(wadsleyite & ringwoodite) preferred phases!!



Resolution interval: $P \leq 22$ GPa T = 0 – 2000 K

Conclusion: wadsleyite II is mechanically stable but not thermodynamically

Conlusions

- Crystal lattice of **wadsleyite II** is mechanically stable up to 30 GPa
- **Wadsleyite II** is thermodynamically unstable in the magnesium-orthosilicate system and can be considered as an intermediate phase
- **Wadsleyite II** structure could be stabilized by Fe ions doping

Thank you.