Mineralogy and Crystal Chemistry

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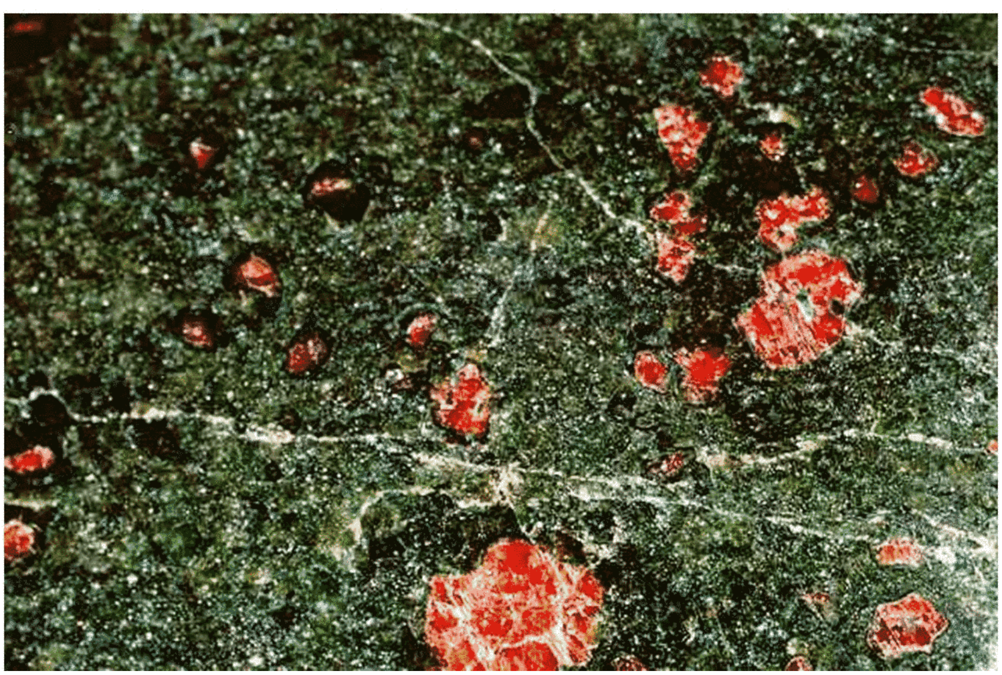
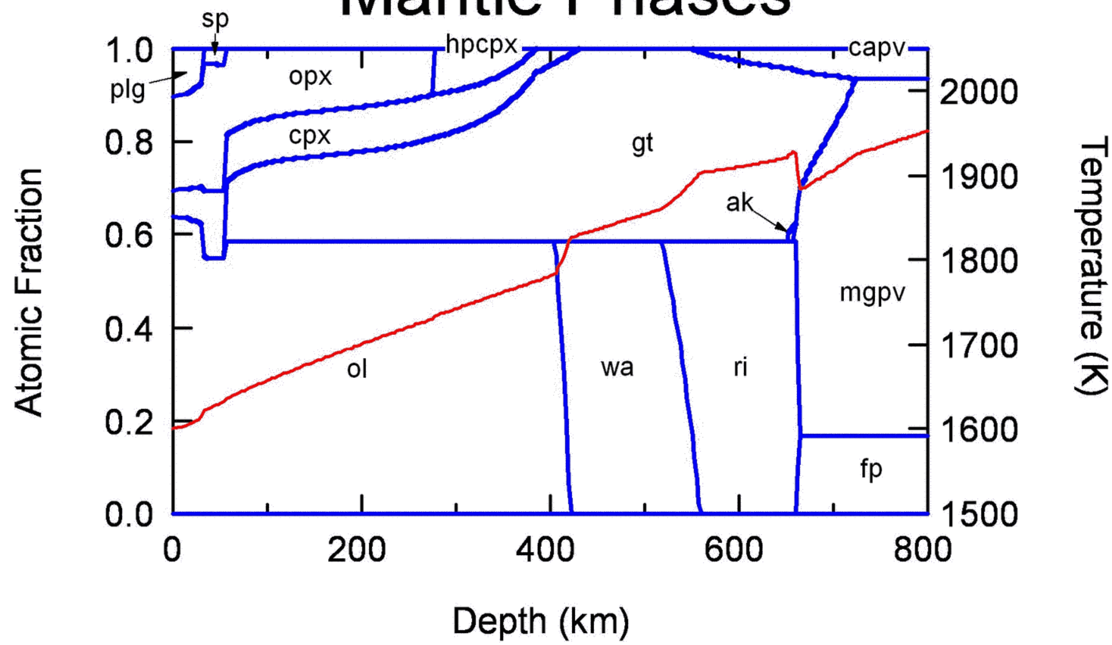
Upper Mantle Xenolith, Depth ~ 100 km

Red=garnet (gt); black=orthopyroxene (opx); green=clinopyroxene (cpx); yellow-green=olivine (ol)

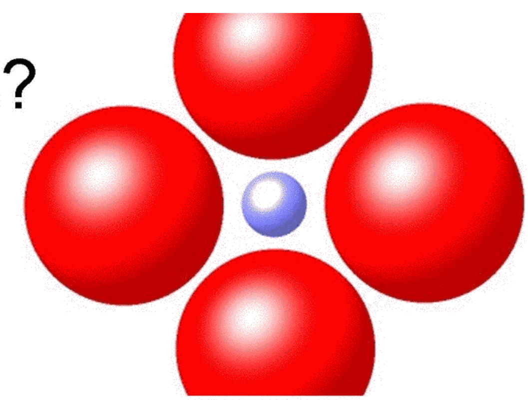


Mantle Phases

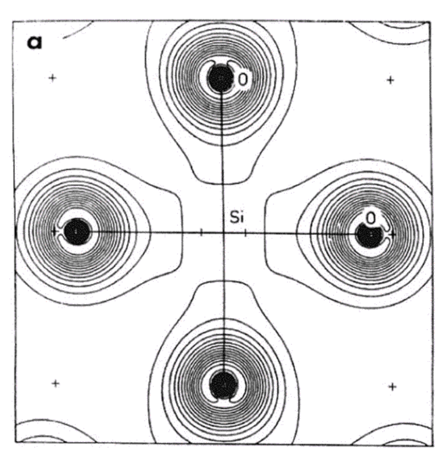


Wadsleyite (wa); Ringwoodite (ri); akimotoite (ak); Mg-perovskite (mgpv); Ca-perovskite (capv); Ferropericlase (fp)

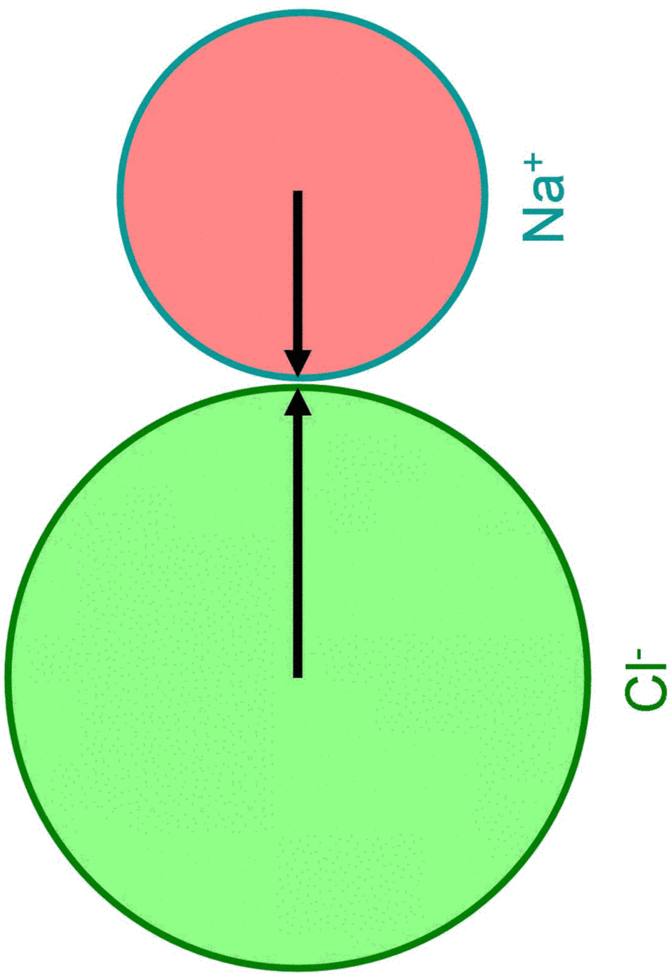
Ions or electrons?



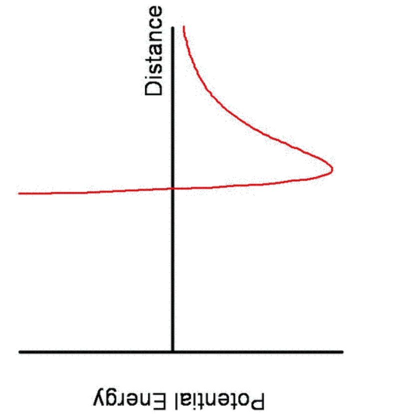
- Pauling/Goldschmidt Model
  - Hard fully charge spheres
  - Rationalize/predict low pressure structures
- High pressure?
  - P_{bond}~eV/Å^3=160 GPa~P_{mantle}
  - Ions change
    - Size
    - Shape
    - Charge

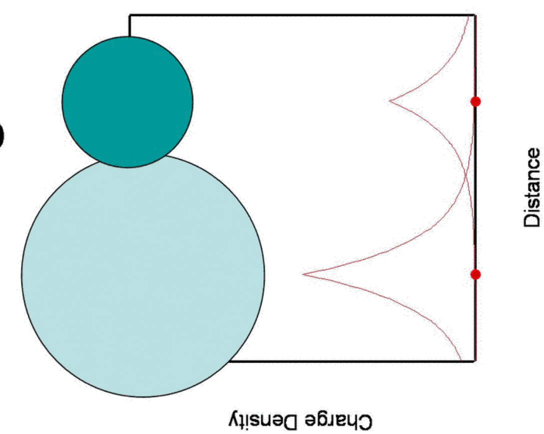


Pauling/Goldschmidt Model



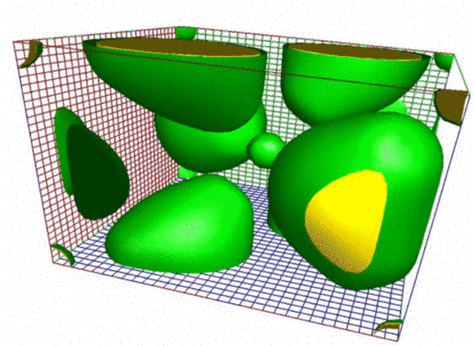
Quantifying the Pauling/Goldschmidt Model





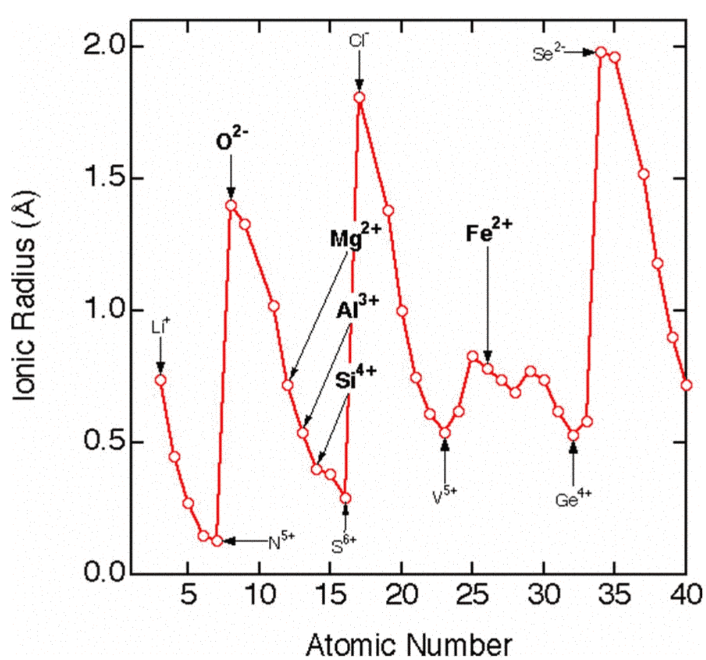
Density functional theory

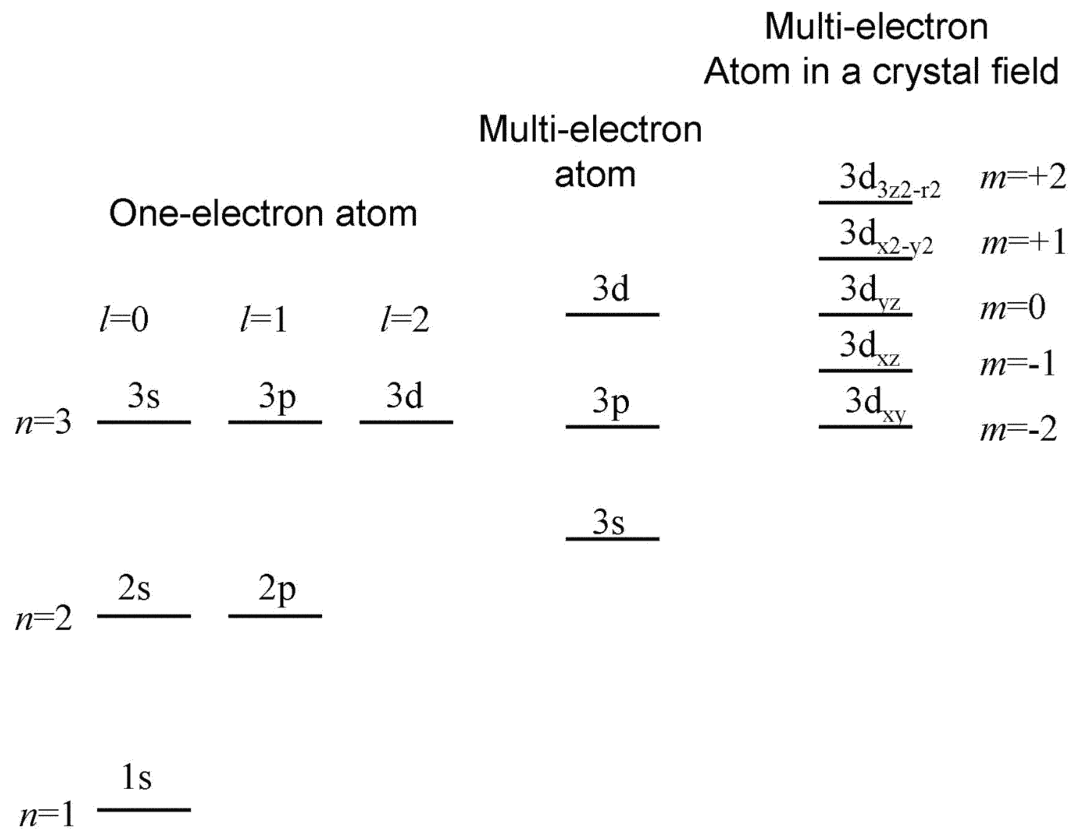
- No assumption about charge density, type of bonding, …
- No experimental input, i.e. no free parameters
- Positions and charges of nuclei.
- Assumption of nuclear positions is generally relaxed
- Not exact



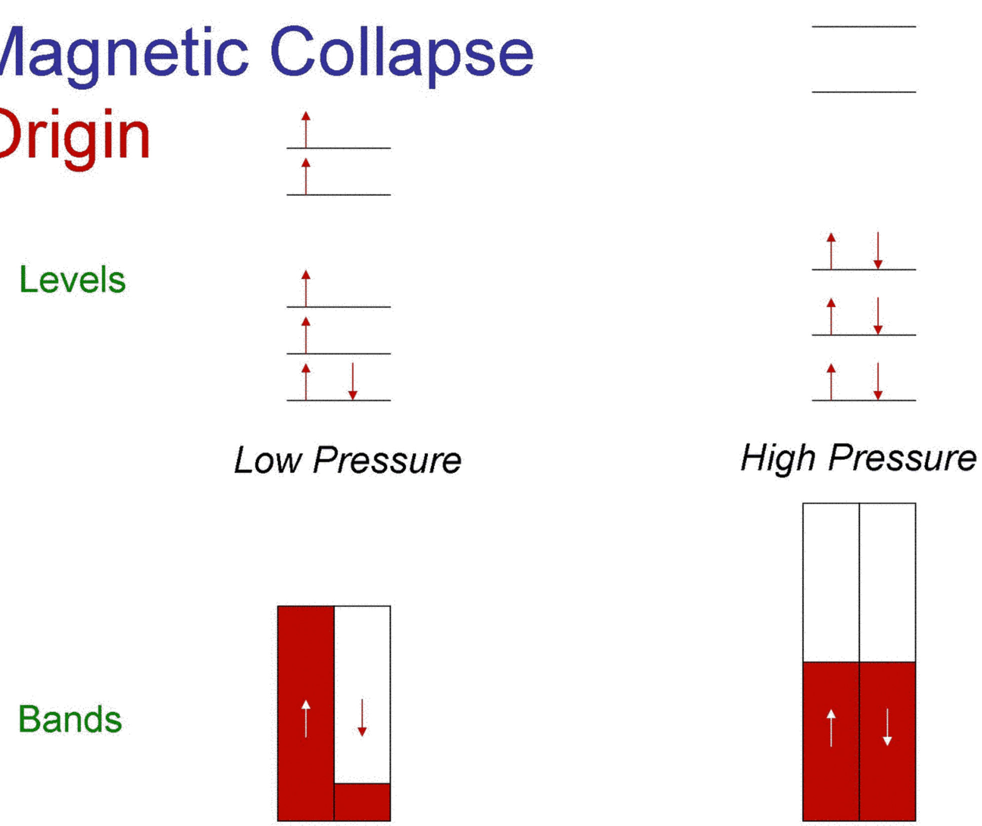
Cohen, 1992

Ionic Radii Shannon and Prewitt



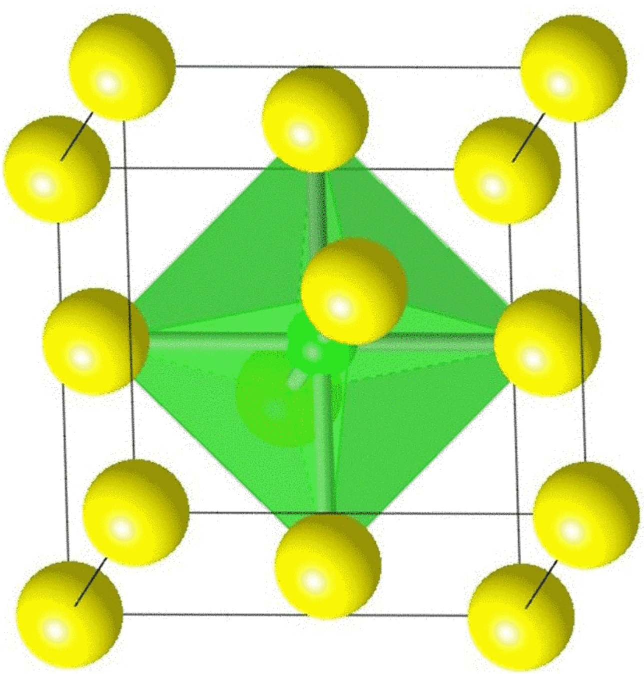


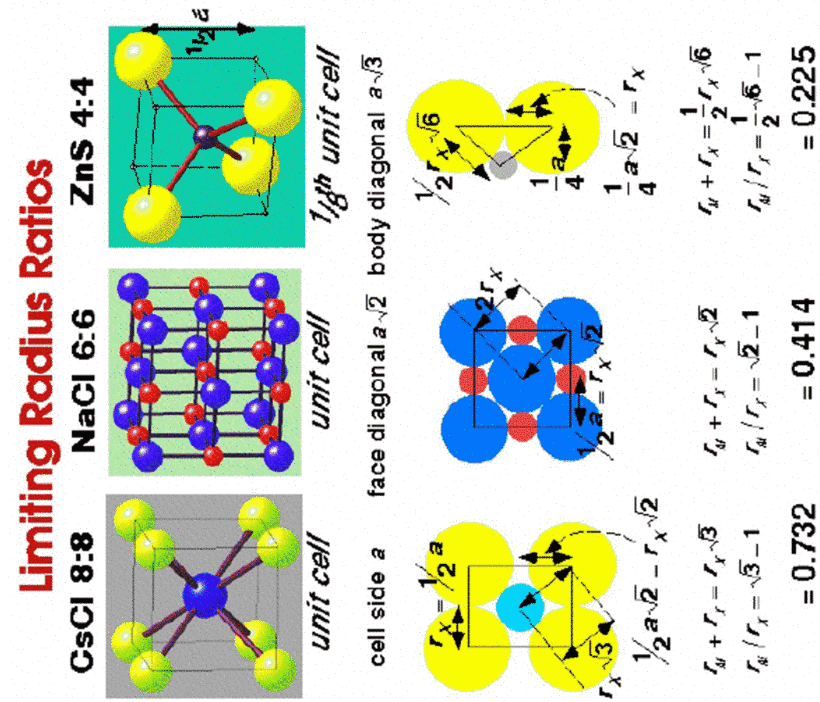
Magnetic Collapse
Origin



Coordination Polyhedra

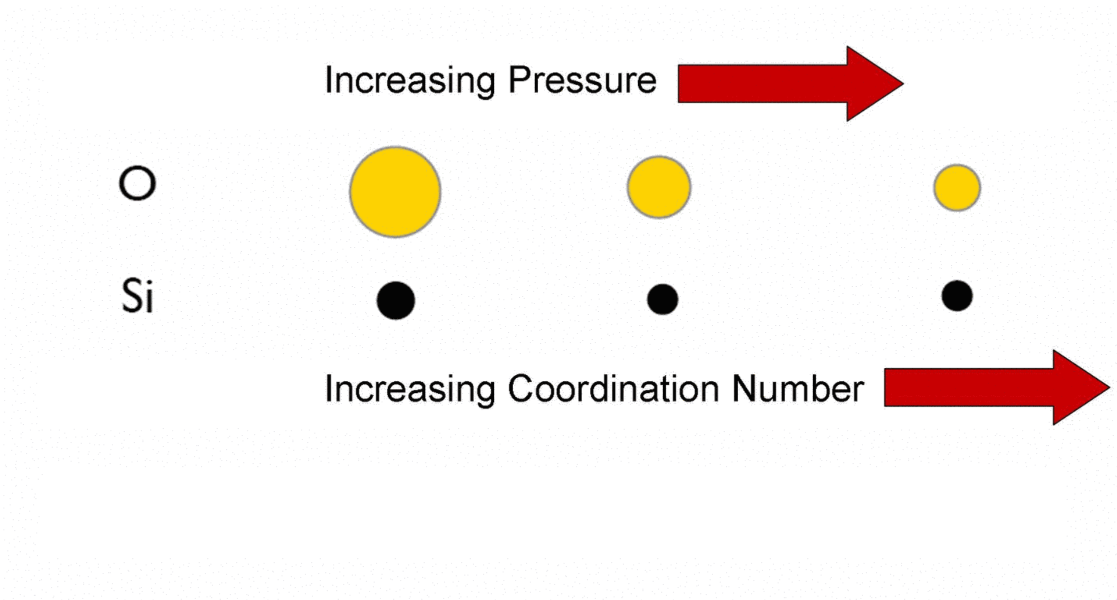
Halite, NaCl



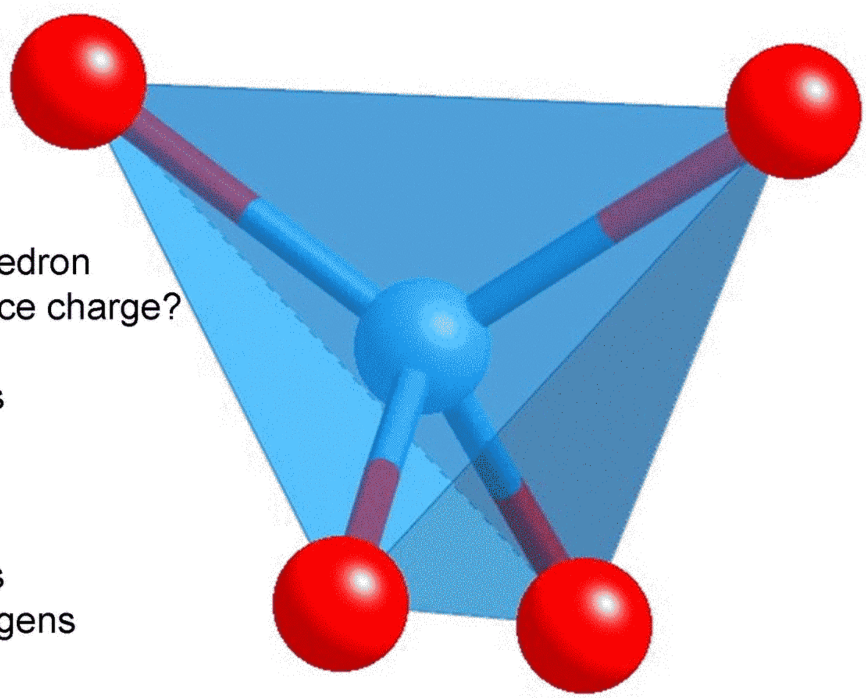


Pressure-Induced Coordination Change

- More Efficient Packing
- Ionic Compressibility



Charge Neutrality

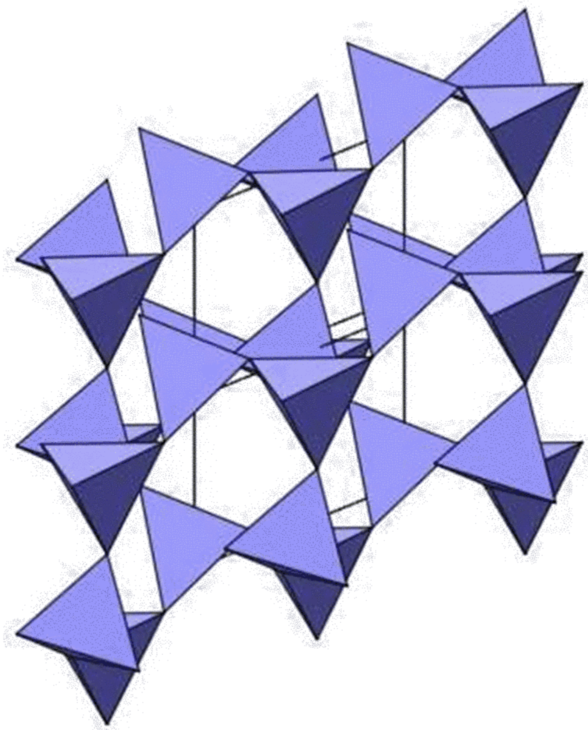


SiO_4^{4-} Tetrahedron
How to balance charge?

Orthosilicates
Add cations
e.g. Mg_2SiO_4

Tectosilicates
Share all oxygens
e.g. SiO_2

Charge Neutrality, Sharing of Elements



Quartz, SiO_2
Shared corners

Pauling's Rules
2. Electrostatic Valency

e.v. = z/n

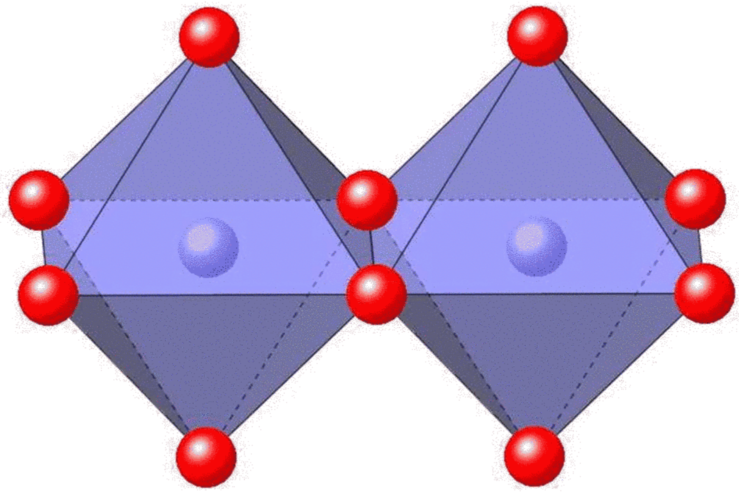
e.v. electrostatic valency
z = ionic charge
n = coordination number

Electrons Transferred
Cations -> Coordinating Anions

How many electrons? z
To how many anions? n
e.v. a measure of bond strength

Isodesmic
Anisodesmic

Charge Neutrality, Sharing of Elements



Stishovite, SiO_2
Shared Edges (and corners)

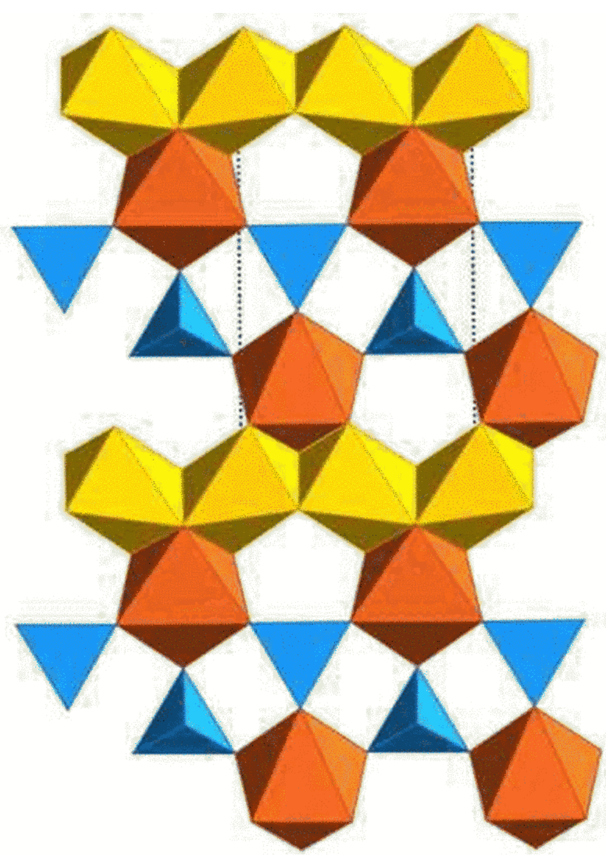
Olivine, Mg_2SiO_4

Mg-octahedra: yellow, orange
Si-tetrahedra: blue

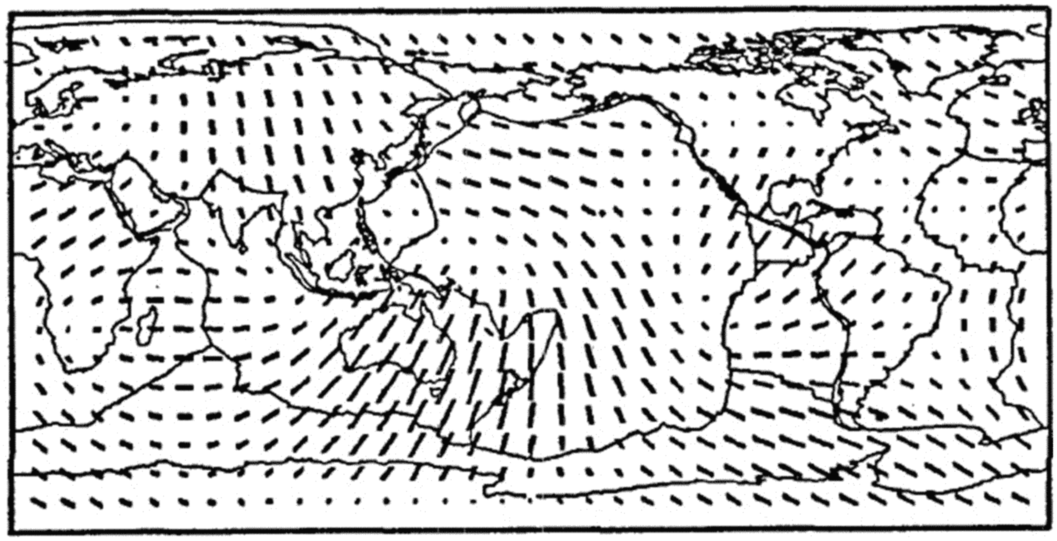
Tetrahedra are isolated, i.e. do not share elements with other tetrahedra

Characteristic of orthosilicates

Also includes garnet



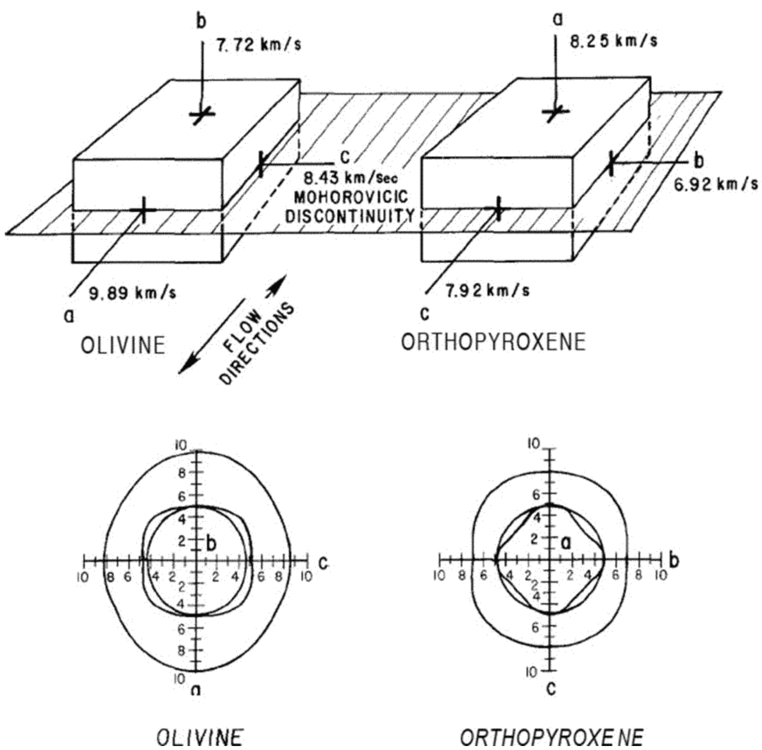
Upper Mantle Azimuthal Anisotropy



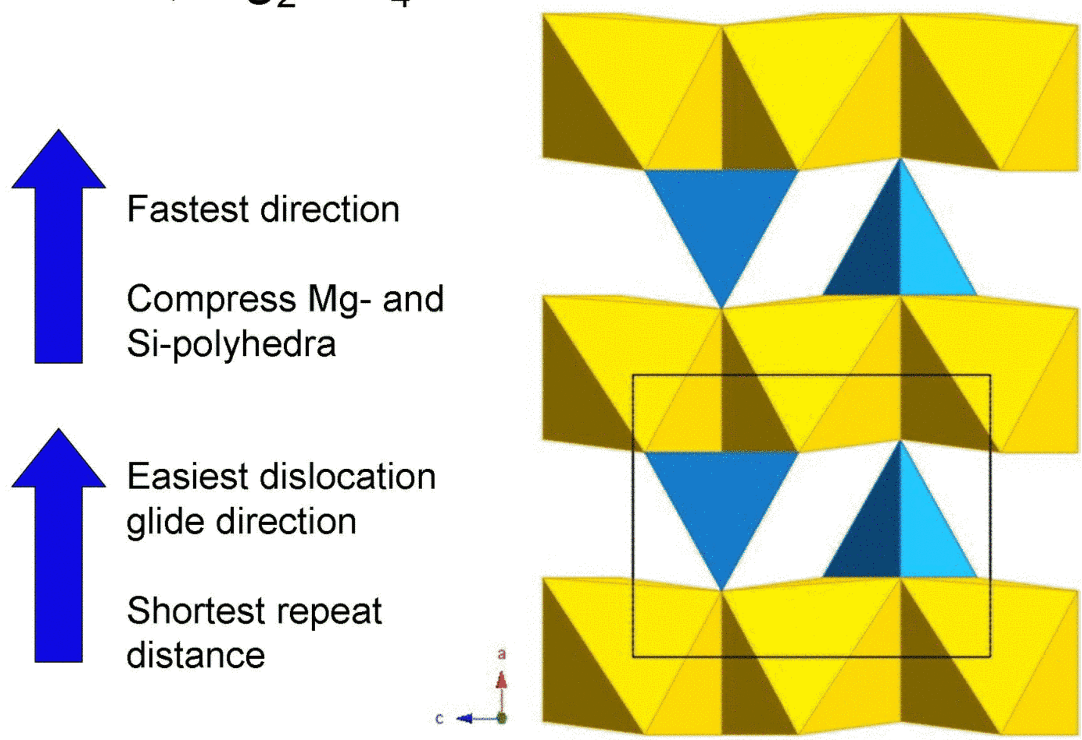
Fast Direction ~ Flow Direction

Tanimoto and Anderson (1984)

Anisotropy and Deformation of Olivine

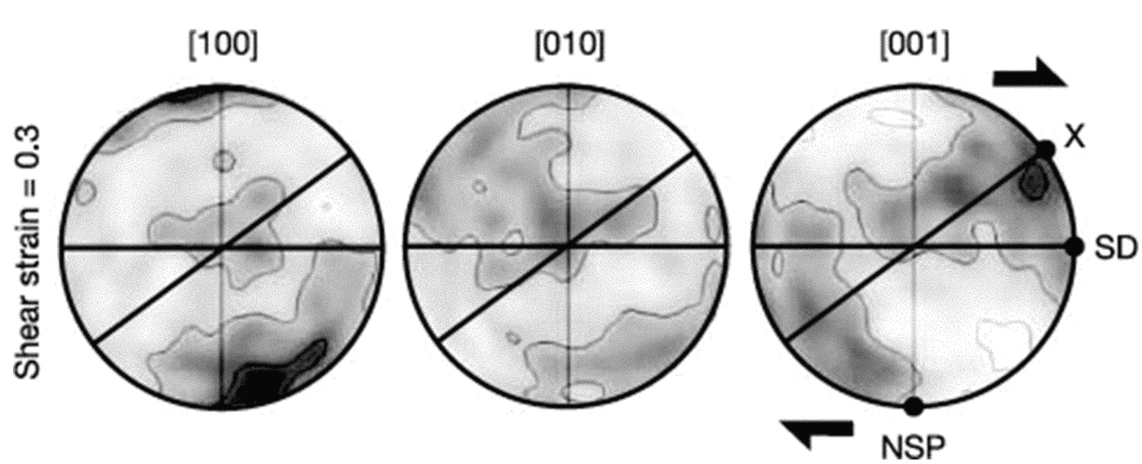


Olivine, Mg_2SiO_4

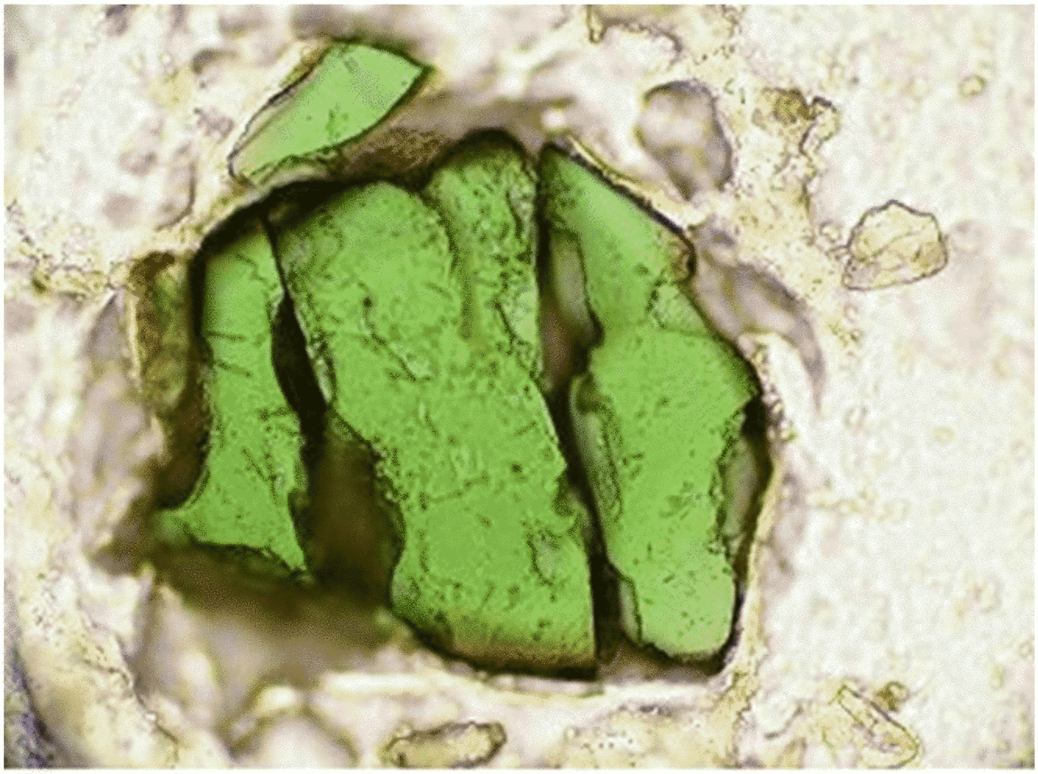


Olivine at 11 GPa (~300 km depth)

Easy slip along c!
Fastest direction perpendicular to flow!



Mainprice et al. (2005)



Synthetic wadsleyite II

Wadsleyite, Mg_2SiO_4

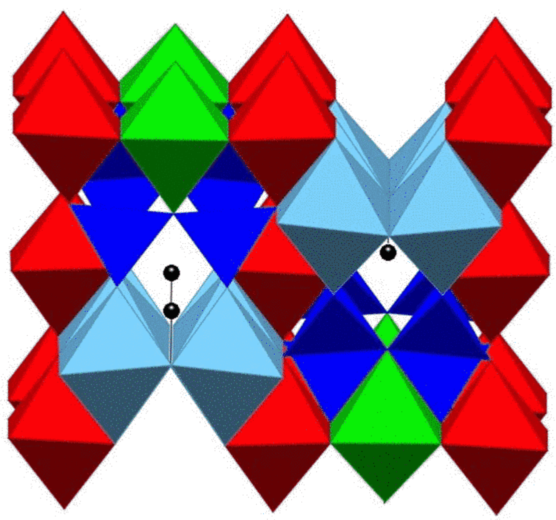
Pairs of tetrahedra share corners

Like sorosilicates (e.g. epidote)
But wrong composition!

Underbonded oxygen
2/6 electrons from each of five
Mg = -5/3 < -2

Ideal place for a hydrogen
Charge balanced by Mg vacancies

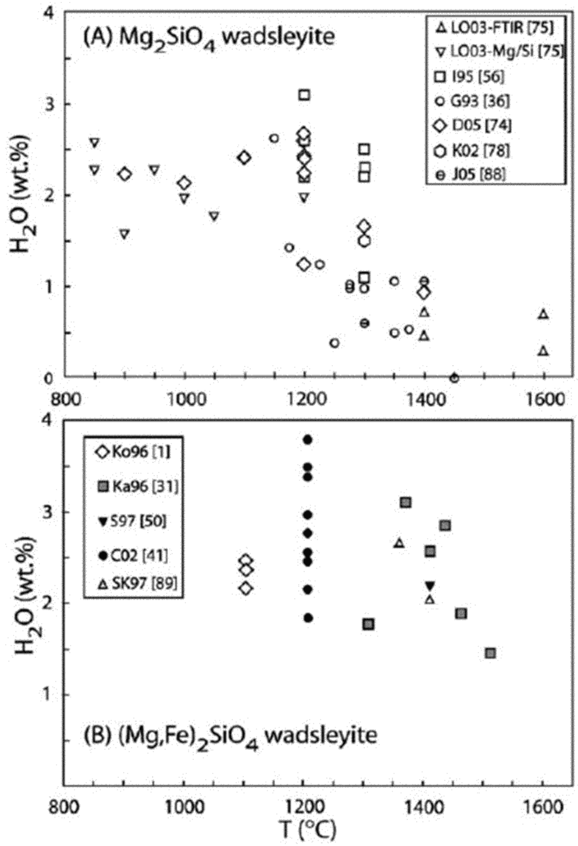
Smyth (1994)



Water solubility in wadsleyite
Hirschmann et al. (2005)

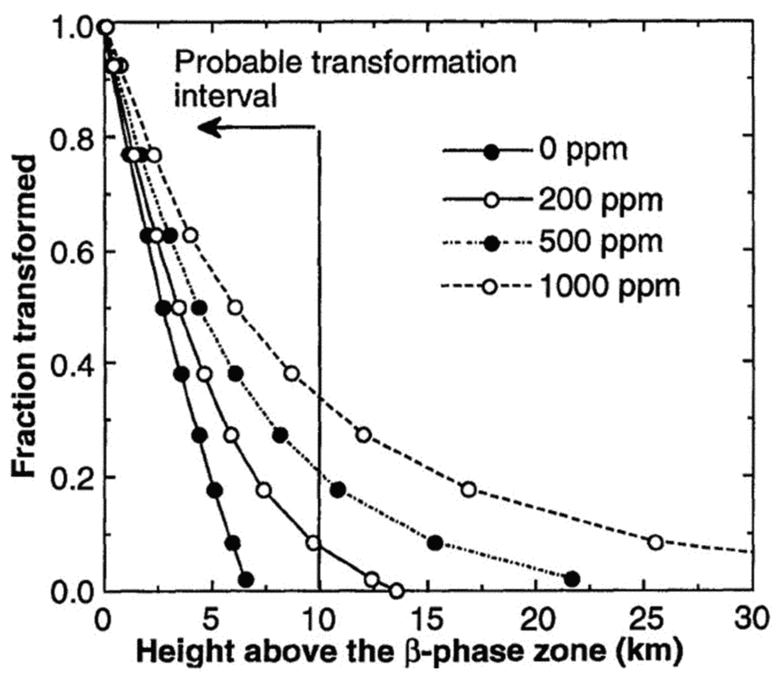
Several weight %

Several oceans if fully hydrated



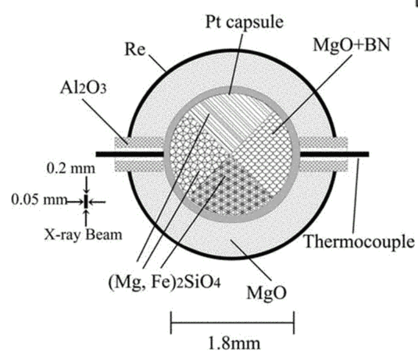
Detection of Water?

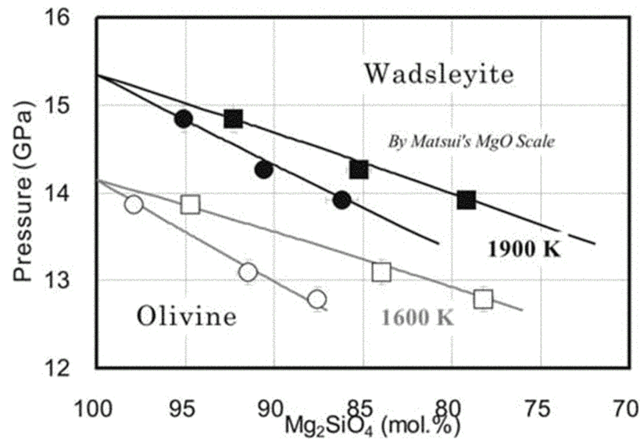
Wood (1995)



Olivine to Wadsleyite Transition

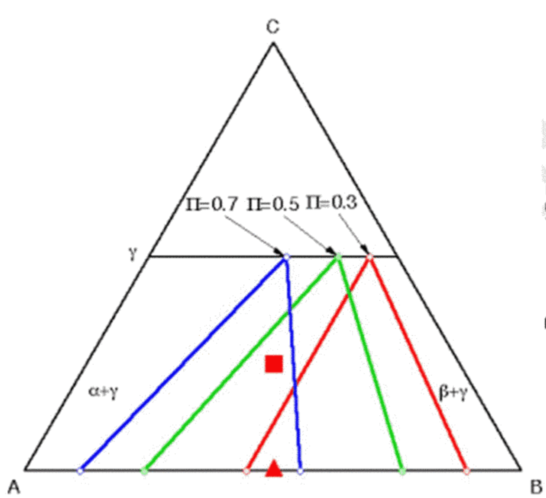
- Mg_2SiO_4-Fe_2SiO_4 System



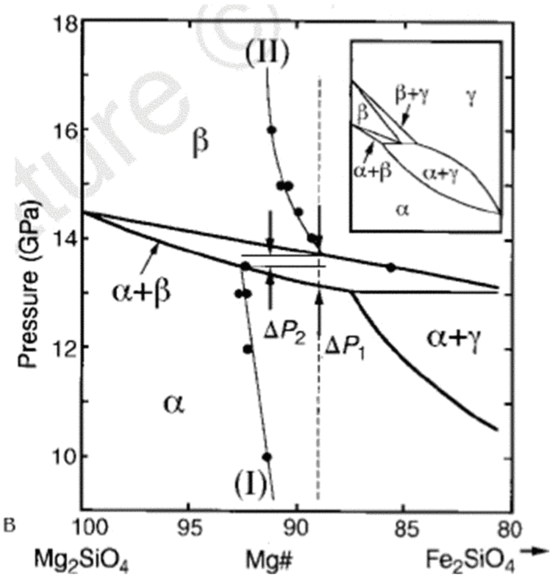


Katsura et al. (2004) GRL

Sharpness of the 410 km discontinuity



Stixrude (1997)



Irifune and Isshiki (1998)

Garnet

$Mg_3Al_2Si_3O_{12}$
8-, 6-, 4-coordinated sites
Garbage can!

Dissolves pyroxenes

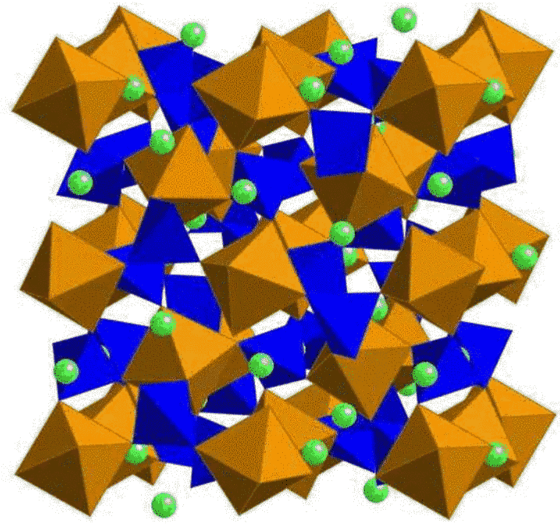
$MgSiO_3$

$Mg_4Si_4O_{12}$

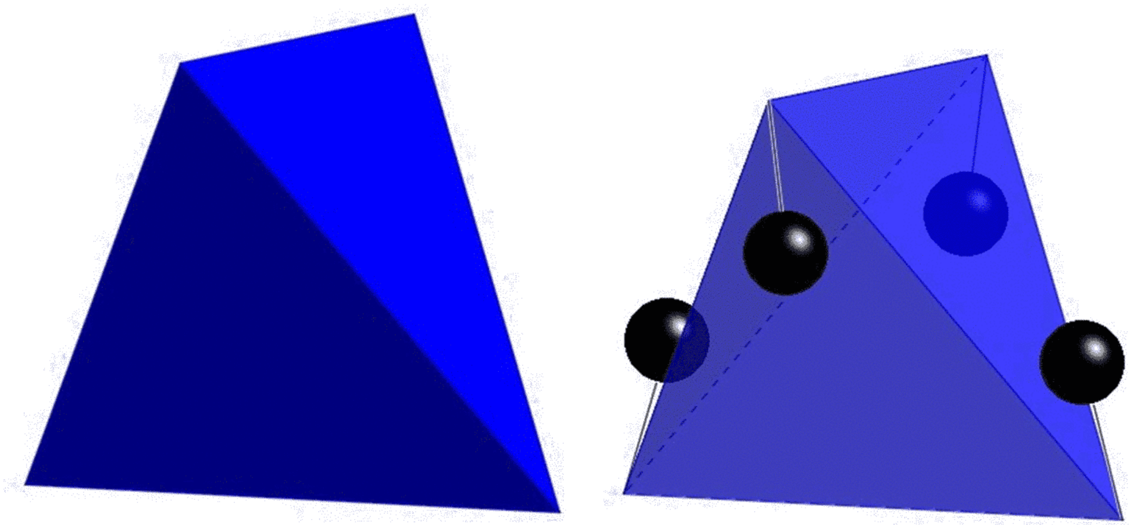
$Mg_3MgSiSi_3O_{12}$

$Mg_3(Mg,Si,Al)_2Si_3O_{12}$

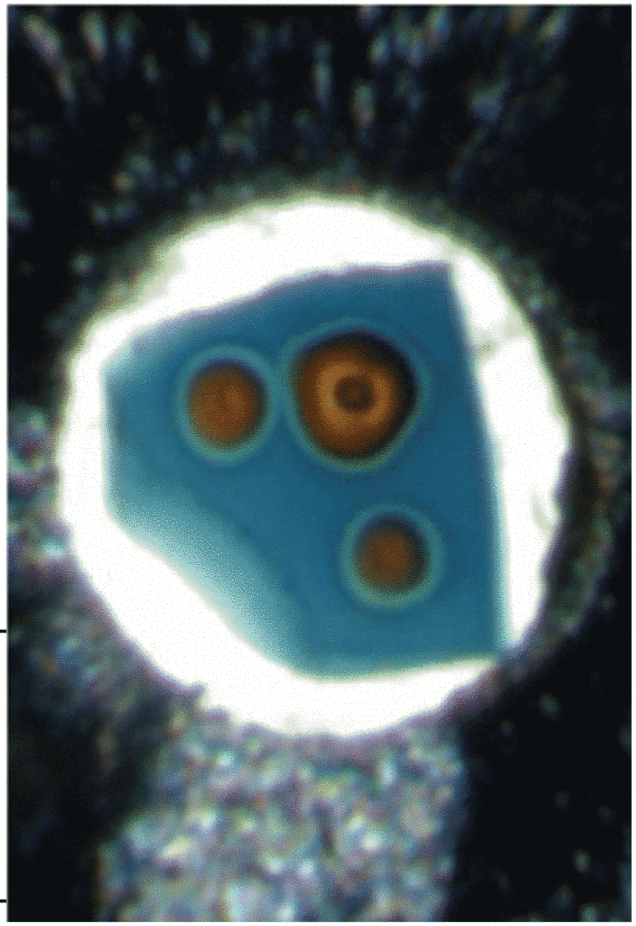
i.e. some Si in 6-fold site



Water in Garnet

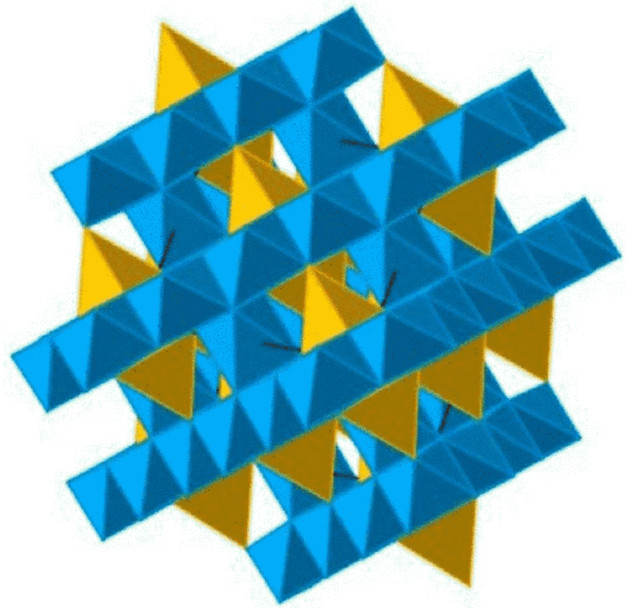


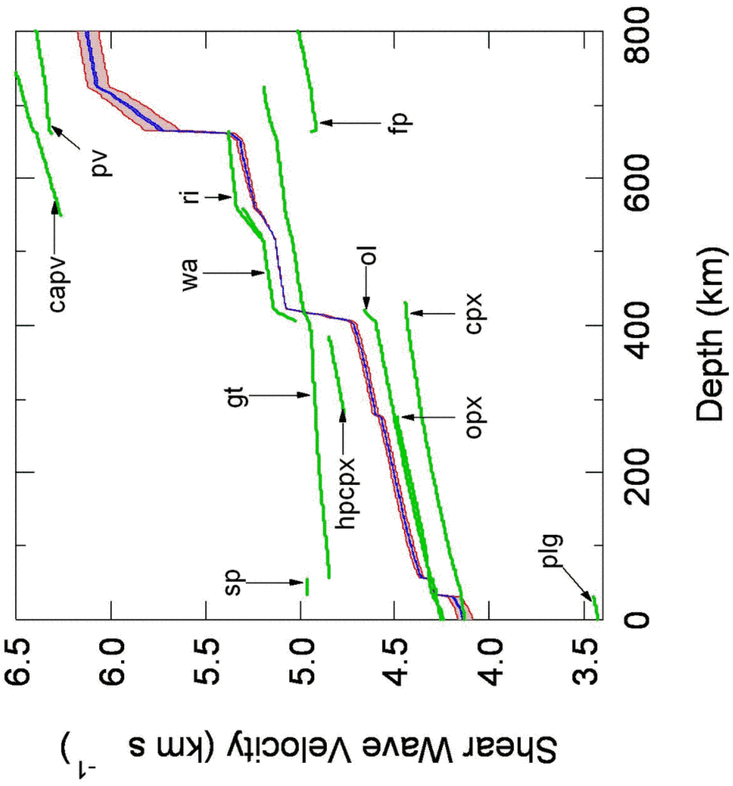
Blue hydrous ringwoodite viewed in situ through the diamond anvil cell, transformed in laser-heated spots to perovskite+ferropericlase



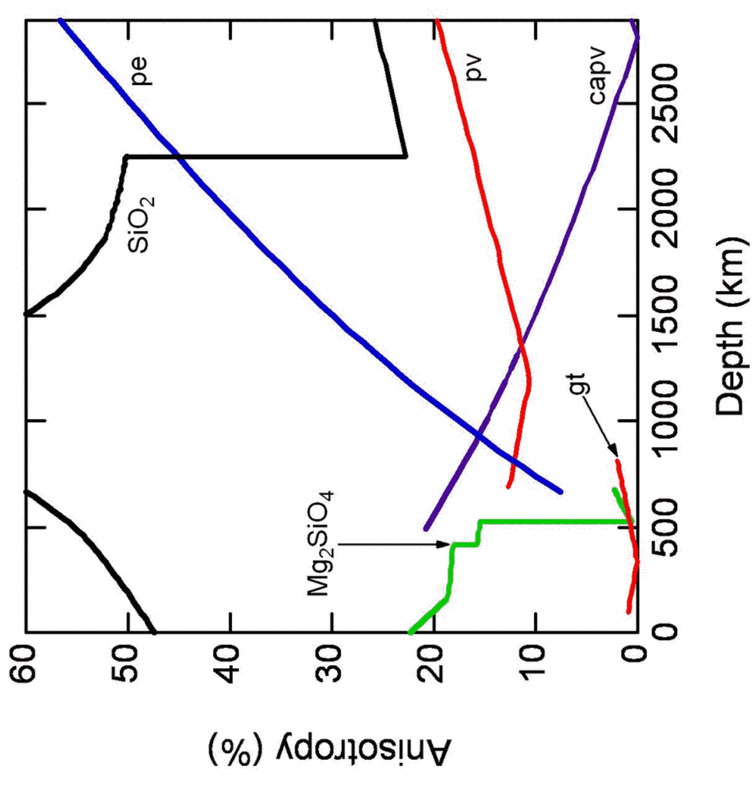
Jacobsen and Lin (2005)

Ringwoodite





Stixrude (2006) Treatise on Geophysics



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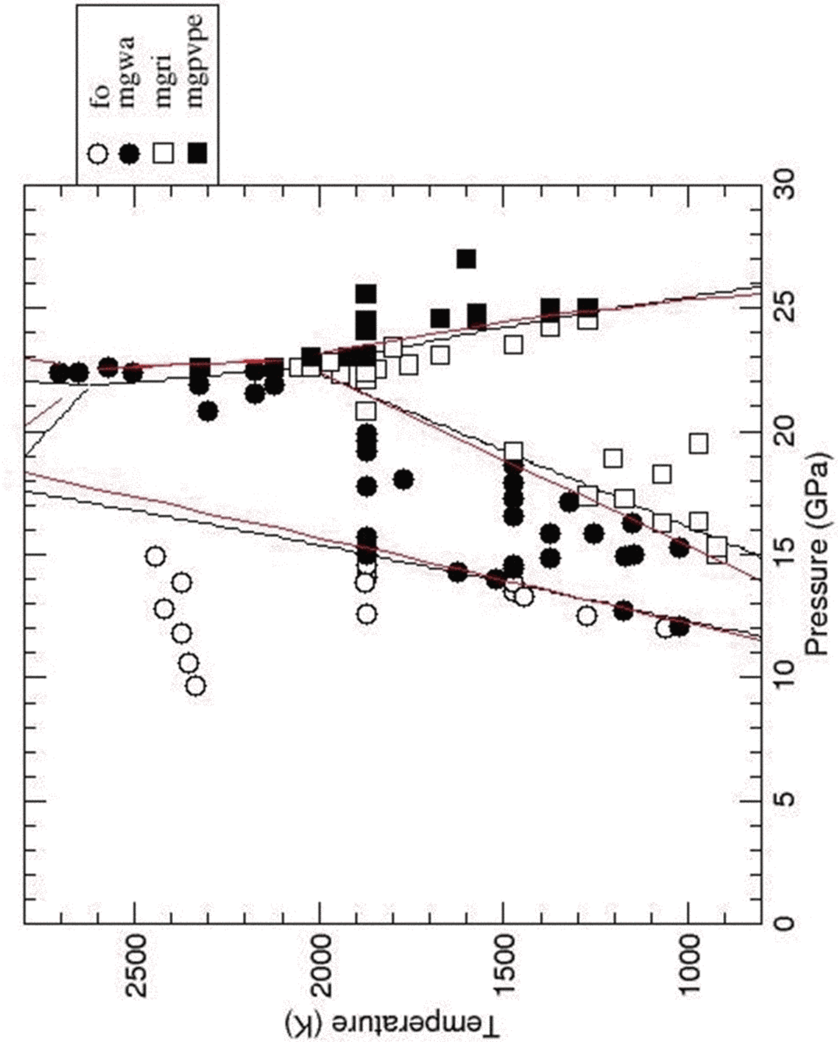
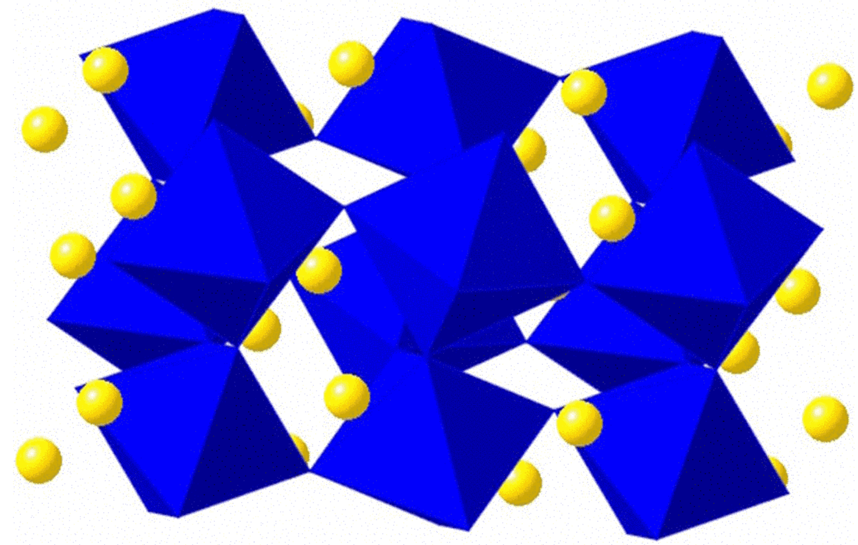

fo
mgwa
mgri
mgpvpe
Temperature (K)
Pressure (GPa)
2500
2000
1500
1000
0
5
10
15
20
25
30



Pervoskite