Phase transitions in Earth’s Mantle and Mantle Mineralogy

Upper Mantle Minerals: Olivine, Orthopyroxene, Clinopyroxene and Garnet

~13.5 GPa: Olivine $\rightarrow$ Wadsrlyite ($\alpha$–$\beta$) transition (ONSET TRANSITION ZONE)

~15.5 GPa: Pyroxene component gradually dissolve into garnet structure, resulting in the completion of pyroxene-majorite transformation

>20 GPa: High CaO content in majorite is unfavorable at high pressure, leading to the formation of CaSiO$_3$ perovskite

~24 GPa: Division of transition zone and lower mantle. Sharp transition silicate spinel to ferromagnesium silicate perovskite and magnesiowustite

>24 GPa: Most of Al$_2$O$_3$ resides in majorite at transition zone pressures, a transformation from Majorite to Al-bearing orthorhombic perovskite completes at pressure higher than that of post-spinel transformation

Lower Mantle Minerals: Orthorhobic perovskite, Magnesiowustite, CaSiO$_3$ perovskite

~27 GPa: Transformation of Al and Si rich basalt to perovskite lithology with assemblage of Al-bearing perovskite, CaSiO$_3$, stishovite and Al-phases
Upper Mantle: olivine, garnet and pyroxene
Transition zone: olivine (a-phase) transforms to wadsleyite (b-phase) then to spinel structure (g-phase) and finally to perovskite + magnesio-wüstite. Transformations occur at P and T conditions similar to 410, 520 and 660 km seismic discontinuities
Xenoliths: (mantle fragments brought to surface in lavas)
60% Olivine + 40 % Pyroxene + some garnet
Garnet: \( A_3B_2(SiO_4)_3 \) Majorite

\( FeSiO_4, (Mg,Fe)_2 SiO_4 \) Germanates (Co-, Ni- and Fe- containing olivines
MgSiO_4, Olivine (ALPHA)
10 GPa = 300 Km Mantle

\( \beta-Mg_2SiO_4 \) Wadsleyite [beta-spinel]
Cr-Mg_2SiO_4 Chromium doped Forsterite

Spinel group \( AB_2O_4 \) [MgAl_2O_4] (GAMMA)
A: divalent Mg, Fe, Ni, Mn, Zn
B: trivalent Al, Fe, Cr, Mn (possibly Ti^{4+} or Pb^{2+})

410 km discontinuity: Alpha \( \rightarrow \) Beta transition responsible for this seismic velocity discontinuity in mantle

660 km discontinuity: divides lower mantle and transition zone (dissociation of ferromagnesium silicate spinel to denser mineral assemblage (20 GPa)
\( Mg_2SiO_4-Fe_2SiO_4 \rightarrow MgSiO_3-FeSiO_3 \)
\( (Mg,Fe)_2SiO_4 \) (Gamma spinel ringwoodite) \( \rightarrow \) \( (Mg,Fe)SiO_3 + (Mg,Fe)O \)
Review of High pressure techniques used for phase equilibrium study
High pressure experimental study on chemical systems

\[ \text{SiO}_2 \]
\[ \text{Mg}_2\text{SiO}_4 \]
\[ \text{Fe}_2\text{SiO}_4 \]
\[ \text{MgSiO}_3 \]
\[ \text{FeSiO}_3 \]
\[ \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} \]
\[ \text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} \]
\[ \text{CaSiO}_3 \]
\[ \text{CaMgSi}_2\text{O}_6 \]

Review Experimental results on mantle peridotite compositions and high pressure phase transformations in the systems related to subducted oceanic lithosphere

**Piston Cylinder Apparatus**
For phase equilibrium measurements under crust and mantle conditions (up to 130 km)

**Multianvil Apparatus (MAIN FOCUS OF THIS PAPER)**
To extend the range of study up to transition zone (750 km)
Features: Eight WC cubes with truncated corners separated from one another by compressible pyrophyllite gasket. Sample placed in a furnace assembly that fits into a hole in the center of octahedron formed by corners of truncated WC cube.

**LHDAC**
This cover whole mantle range but it suffers from a large thermal gradient, small sample size and achieving equilibrium
Olivine

One of major content and studied extensively because of its connection to 410 and 660 km Discontinuities.

Three polymorphs of Mg$_2$SiO$_4$:
Olivine
β-phase (Wadselyite)
γ-Spinel or Ringwoodite

Discrepancies in determination of phase boundaries because if difference in pressure scale at high temperature

Spinel $\rightarrow$ Perovskite + MgO
22-25 GPa at Room temperature

23 GPa at RT
<21 GPa at RT (After temperature correction To the pressure)
Quartz

Common Crustal Mineral
Quartz $\rightarrow$ Coesite 3 GPa
Coesite $\rightarrow$ Stishovite 9 GPa
Stishovite $\rightarrow$ Dense CaCl$_2$ type structure 50 GPa
Post Stishovite phases $\rightarrow$ >50 GPa

Discrepancy in $\alpha$–$\beta$-coesite triple point from the correction for friction in piston cylinder apparatus

Coesite has been found in ultra high pressure metamorphic rock and as mineral inclusion in eclogite diamond host rocks were subjected to pressures equivalent to depth of ~ 80 – 100 km

No stishovite in metamorphic/igneous rock
Except in shocked rocks and metrorites
Its formation requires host rock to be deeper than 300km
Fe$_2$SiO$_4$

Direct transformation from Olivine to $\gamma$-spinel

Phase boundary between
1073 – 1473 K

Post spinel transition reported at 17.3 GPa with no apparent temperature dependence

Transition Pressure =
2.75 + 0.0025T (C)
Phase Relation between $\text{Mg}_2\text{SiO}_4$ and $\text{Fe}_2\text{SiO}_4$

No wadsleyite in Fe2SiO4, therefore (Mg,Fe)2SiO4 wadsleyite solid solution does not extend to Fe-rich region.

Max. solubility FeO in wadsleyite structure is 28 mol% at 1600 C
Composition of coexisting $\alpha$ and $\beta$ phases at three pressures

Compression and Reversal points and shows that the calibration of apparatus was very good

At 13, 13.45 and 13.9 GPa the composition of $\alpha$ and $\beta$ phase vary linearly with P and intersect at 14.6 GPa and $\text{Mg}_2\text{SiO}_4$ composition

Reversal expt. 12.9, 13.35 GPa from pre-synth. $\beta$-phase and olivine
Coexisting $\alpha$-phase has $\text{Fe}/\text{Fe+Mg} = 0.118$ and 0.111
Using $\alpha$ and $\beta$ as start mat.
Coexisting $\text{b}$-phase comp. are 0.212 and 0.216
Phase Diagram of Mg$_2$SiO$_4$-Fe$_2$SiO$_4$ at 1600 C

(Mg,Fe)SiO$_3$ forms limited solid solution govern by
(Mg,Fe)SiO$_3$ $\rightarrow$ Mg.Fe)O + SiO$_2$
Solubility is function of pressure and temp.

MA expt.: 0.05 at 1000C to 0.12 at 1750 C at 26 GPa

LHDAC expt.: $\sim$28 mol% FeSiO$_3$
can be dissolved into pv at 50 GPa and 1600C

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Six polymorphs of MgSiO$_3$ perovskite:

(1) Protoenstatite: $\rightarrow$ clinoenstatite at 8.1 GPa and 1000C (positive slope)

(2) Orthoenstatite: $\rightarrow$

(3) Clinoenstatite: $\rightarrow$ At high pressure, decomposes to two phase region Wadsleyite + Stishovite or spinel + stishovite region Which separate the phase field of pyroxene and Ilmenite

At 1700 C 17 GPa pyroxene $\rightarrow$ tetragonal Garnet (majorite) $\rightarrow$ perovskite transition not yet determined (> 2000C) Al bearing majorite $\rightarrow$ perovskite has positive slope

(4) Non-cubic garnet

(5) Ilmenite $\rightarrow$ Perovskite at 24.3 GPa and 1000C (negative slope)

(6) Perovskite
Phase relations in perovskite ($\text{MgSiO}_3$) and Pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$):

Phase transformations in Pyrope:
Pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) $\rightarrow$ Ilmenite at 24 GPa and 1000°C
Pyrope $\rightarrow$ Ilmenite $\rightarrow$ Al bearing silicate perovskite $+\text{Al}_2\text{O}_3$ (corundum) at 26 GPa and $>1000$°C
$\text{Al}_2\text{O}_3$ solubility in perovskite increases with pressure
Orthorhombic perovskite with pyrope composition forms: at 37 GPa
Phase Transformation in FeSiO$_3$, Fe$_3$Al$_2$Si$_3$O$_{12}$, CaSiO$_3$, CaMgSi$_2$O$_6$

Ferro sillite FeSiO$_3$: Perovskite, Majorite and Ilmenite are not stable

FeSiO$_3$ $\rightarrow$ Fe$_2$SiO$_4$ (spinel) + SiO$_2$ (Stishovite) at 10 GPa $\rightarrow$ Fe$_x$O (Wustite) + SiO$_2$ (stishovite) at 17.3 GPa

MgSiO$_3$ - FeSiO$_3$ phase diagram shows: pyroxene-spinel-stishovite and spinel-magnesiowustite-stishovite loop in Fe-rich region and complex phase relations in Mg-rich region

Almandine (Fe$_3$Al$_2$Si$_3$O$_{12}$) $\rightarrow$ wustite + corundum + Stishovite at 21 GPa

Phase diagram of Mg$_3$Al$_2$Si$_3$O$_{12}$ - Mg$_3$Al$_2$Si$_3$O$_{12}$ not experimentally determined

- Interpretation from phase relations of end members indicates that solubility of FeO in Al-bearing perovskite is limited
- Change of Al$_2$O$_3$ solubility in perovskite at pressure between 26 – 37 GPa

Like MgSiO$_3$ - Mg$_3$Al$_2$Si$_3$O$_{12}$ system, FeSiO$_3$ - Fe$_3$Al$_2$Si$_3$O$_{12}$ also forms solid solution by a heterovalent substitution FeSi – AlAl.

Solubility of FeSiO$_3$ increases in Fe$_3$Al$_2$Si$_3$O$_{12}$ with pressure (max. solubility of 40 mol% at 9 GPa and 1000°C)

Clinopyroxene, garnet, (Ca, Mg) SiO$_3$ and CaSiO$_3$ are major Ca-bearing phases in Earth’s mantle

CaSiO$_3$ appears around 17 – 18 GPa depending on CaO content in bulk composition

Walstromite CaSiO$_3$ $\rightarrow$ Ca$_2$SiO$_4$ + CaSi$_2$O$_5$ at 10 GPa $\rightarrow$ CaSiO$_3$ perovskite at 12 GPa
Diopside $\text{CaMgSi}_2\text{O}_6$ is end member of rock forming pyroxene $\rightarrow \text{CaSiO}_3$ perovskite and $(\text{Ca, Mg})\text{SiO}_3$ majorite at 17-18 GPa and 1300 C or to $\text{CaSiO}_3$ perovskite + MgSiO$_3$ Ilmenite below 1300 C or to $\text{CaSiO}_3$ perovskite + Mg$_2$SiO$_4$ spinel + SiO$_2$ stishovite at 19 GPa and 1500 C [Discrepancy is due to uncertainty in determination phase transformation boundaries because of kinetics and in the pressure scale]

**BULK ROCKS**

Two competing petrological models:

**Pyrolite (peridotite): olivine rich (61% by volume) assemblage**

- Four part dunite + one part basalt......chemical composition in Table 2

**Piclogite: Clinopyroxene-garnet riee, olivine bearing rock (< 50% by vol. olivine)**

- From seismic data: 40% olivine + 37% c-pyroxene+13% garnet+10% o-pyroxene
- Sound velocity date: 38-50% olivine in upper mantle is reqd. to satify 410 km discontinuity (uncertainty due to temp. effect on velocity contrast)

410 km discontinuity 13-16 GPa in peridotite composition depending on temperature & 13-16 GPa and 1380 C in pyroilitic composition
Fig. 16. Melting and sub-solid phase relations in MORB composition at high pressures and temper-