Phase transitions in Earth's Mantle and Mantle Mineralogy

Upper Mantle Minerals: Olivine, Orthopyroxene, Clinopyroxene and Garnet

~13.5 GPa: Olivine → 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_2O_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

β-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 → 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 → $MgSiO_3$-$FeSiO_3$
$(Mg,Fe)_2SiO_4$ (Gamma spinel ringwoodite) → $(Mg,Fe)SiO_3$ + $(Mg,Fe)O$

Review of High pressure techniques used for phase equilibrium study
High pressure experimental study on chemical systems
SiO_2
Mg_2SiO_4
Fe_2SiO_4
$MgSiO_3$
$FeSiO_3$
$Mg_3Al_2Si_3O_{12}$
$Fe_3Al_2Si_3O_{12}$
$CaSiO_3$
$CaMgSi_2O_6$
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_2SiO_4:
Olivine
β-phase (Wadselyite)
γ-Spinel or Ringwoodite

Image removed due to copyright considerations.

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

Spinel → 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 → Coesite 3 GPa
Coesite → Stishovite 9 GPa
Stishovite → Dense $CaCl_2$ type structure
50 GPa
Post Stishovite phases → >50 GPa

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

Image removed due to copyright considerations.

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_2SiO_4

Direct transformation from Olivine to γ-spinel

Phase boundary between 1073 – 1473 K

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

Image removed due to copyright considerations.

Transition Pressure = $2.75 + 0.0025T$ (C)

Phase Relation between Mg_2SiO_4 and Fe_2SiO_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

Image removed due to copyright considerations.

Composition of coexisting α and β phases at three pressures

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

At 13, 13.45 and 13.9 GPa the composition of α and β phase vary linearly with P and intersect at 14.6 GPa and Mg_2SiO_4 composition

Reversal expt. 12.9, 13.35 GPa from pre-synth. β-phase and olivine
Coexisting α-phase has Fe/Fe+Mg = 0.118 and 0.111
Using α and β as start mat.
Coexisting b-phase comp. are 0.212 and 0.216

Image removed due to copyright considerations.

Phase Diagram of Mg_2SiO_4-Fe_2SiO_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. : ~28 mol% FeSiO3 can be dissolved into pv at 50 GPa and 1600C

Image removed due to copyright considerations.

Six polymorphs of $MgSiO_3$ perovskite:

(1) Protoenstatite: → clinoenstatite at 8.1 GPa and 1000C
(positive slope)

(2) Orthoenstatite: →

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

Image removed due to copyright considerations.

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

(4) Non-cubic garnet

(5) Ilmenite → Perovskite at 24.3 GPa and
1000C (negative slope)

(6) Perovskite

Phase relations in perovskite ($MgSiO_3$) and Pyrope ($Mg_3Al_2Si3O_{12}$):

Phase transformations in Pyrope:

Pyrope ($Mg_3Al_2Si_3O_{12}$) → Ilmenite at 24 GPa and 1000C

Pyrope – Ilmenite → Al bearing silicate perovskite + Al_2O_3 (corundum) at 26 GPa and >1000C

Al_2O_3 solubility in perovskite increases with pressure

Orthorhombic perovskite with pyrope composition forms: at 37 GPa

Image removed due to copyright considerations.

Phase Transformation in $FeSiO_3$, $Fe_3Al_2Si_3O_{12}$, $CaSiO_3$, $CaMgSi_2O_6$

Ferrosillite $FeSiO_3$: Perovskite, Majorite and Ilmenite are not stable

$FeSiO_3$ → Fe_2SiO_4 (spinel) + SiO_2 (Stishovite) at 10 GPa → Fe_xO (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 ($Fe_3Al_2Si_3O_{12}$) → wustite + corundum + Stishovite at 21GPa

Phase diagram of $Mg_3Al_2Si_3O_{12}$ - $Mg_3Al_2Si_3O_{12}$ not experimentally determined

-Interpretation from phase relations of end members indicates that solubility of FeO in Al-bearing perovskite is limited

- Change of Al_2O_3 solubility in perovskite at pressure between 26 – 37 GPa

Like $MgSiO_3$ - $Mg_3Al_2Si_3O_{12}$ system, $FeSiO_3$ - $Fe_3Al_2Si_3O_{12}$ also forms solid solution by a hetrovalent substitution FeSi – AlAl.

Solubility of $FeSiO_3$ increases in $Fe_3Al_2Si_3O_{12}$ with pressure (max. solubility of 40 mol% at 9 GPa and 1000C)

Clinopyroxene, garnet, (Ca, Mg) SiO_3 and $CaSiO_3$ are major Ca-bearing phases in Earth's mantle

CaSiO3 appears around 17 – 18 GPa depending on CaO content in bulk composition

Walstromite $CaSiO_3$ → Ca_2SiO_4 + $CaSi_2O_5$ at 10 GPa → $CaSiO_3$ perovskite at12 GPa

Diopside $CaMgSi_2O_6$ is end member of rock forming pyroxene → $CaSiO_3$ perovskite and $(Ca,Mg)SiO_3$ majorite at 17-18 GPa and 1300 C or to $CaSiO_3$ perovskite + $MgSiO_3$ Ilmenite below 1300 C or to $CaSiO_3$ perovskite + Mg_2SiO_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 (perdotite): olivine rich (61% by volume) assemblage

Four part dunite + one part basalt……chemical composition in Table 2

Piclogite: Clinopyroxene-garnet ricg, 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 pyrolitic composition

Image removed due to copyright considerations.

FIG. 16. Melting and sub-solid phase relations in MORB composition at high pressures and temper-