Melting and melts in the deep Earth

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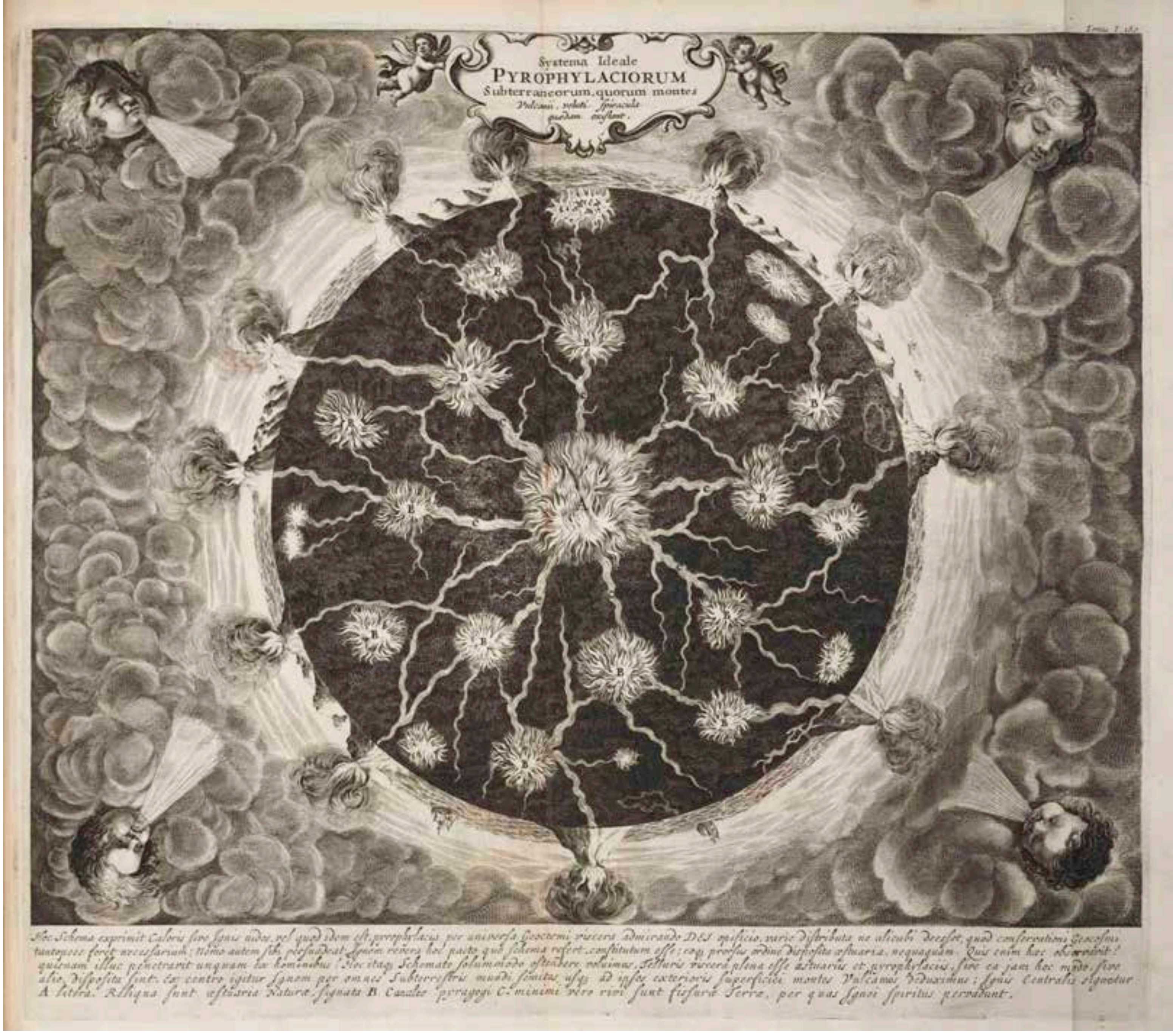
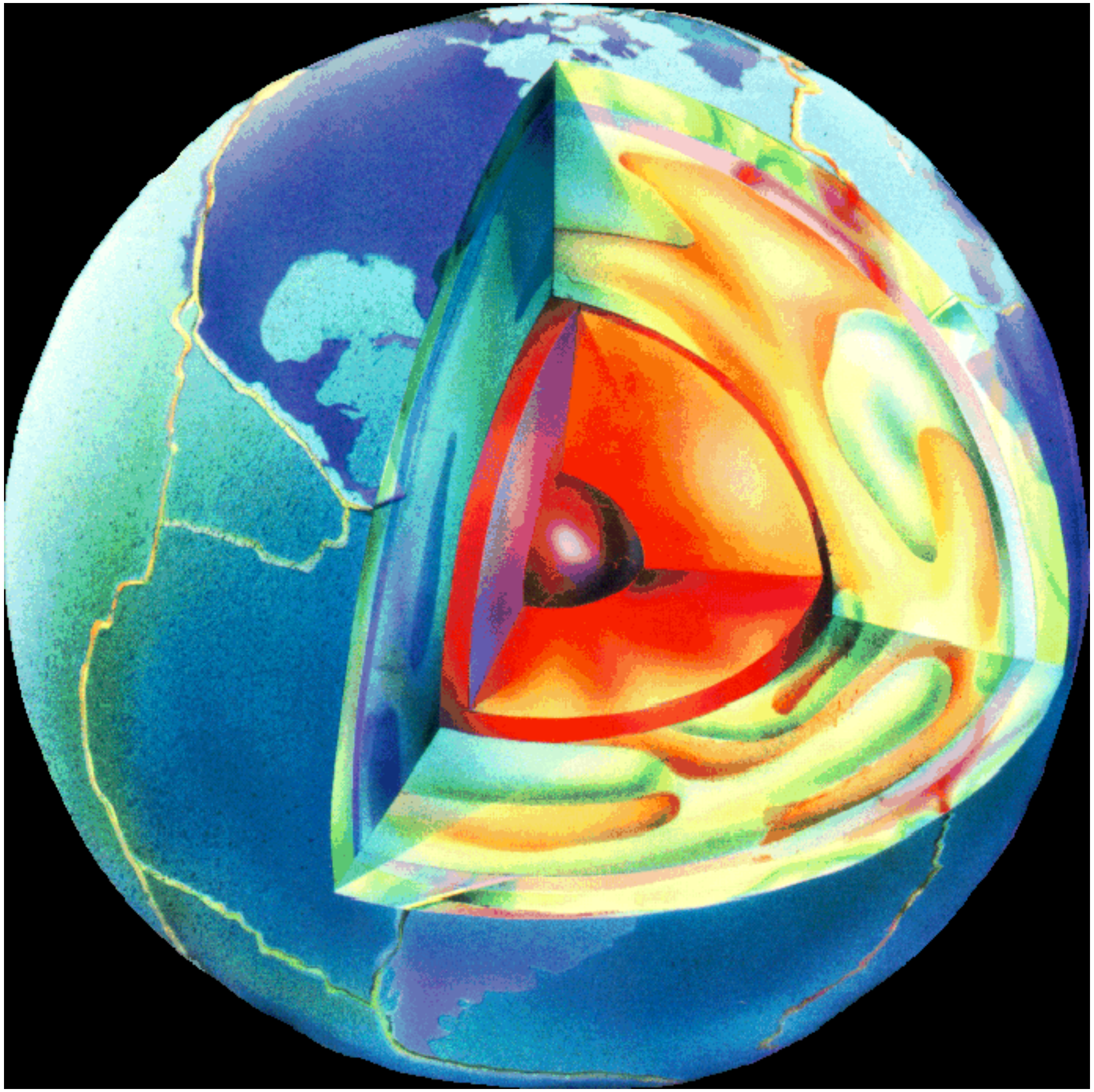
(After CIDER: Southern University of Science and Technology)

Kilauea volcano, Hawaii, Kent Nishimura/LA Times

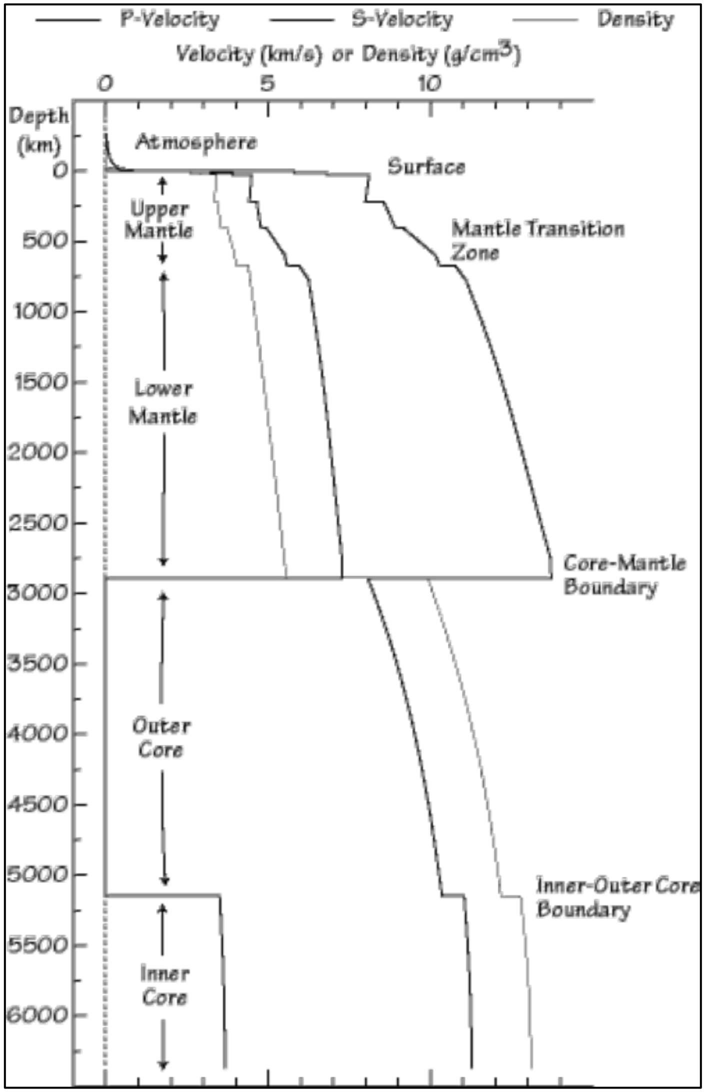


Earth’s internal fires, Athanasius Kircher

Molten layer inside? - Outer core

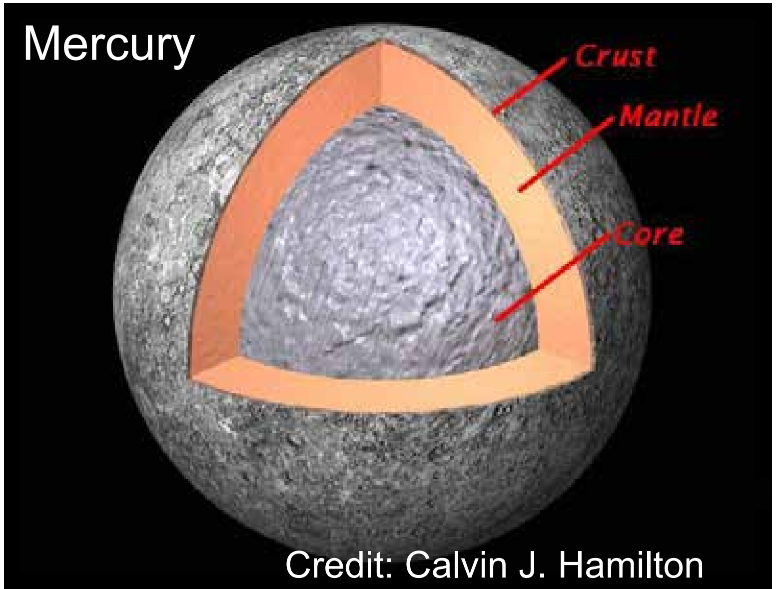


Credit: Keelin Murphy

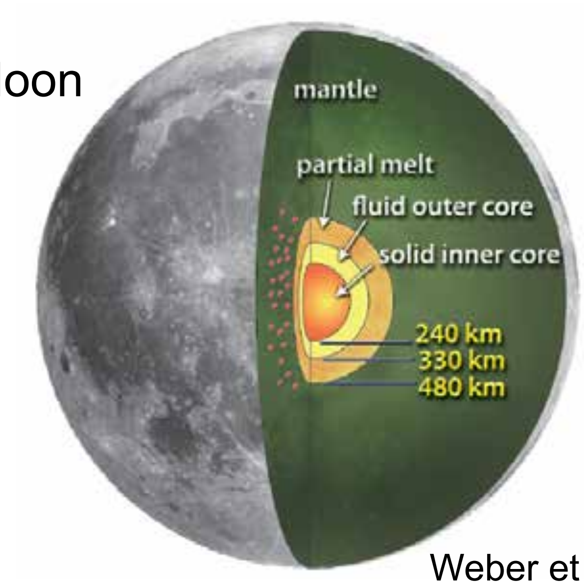


Dziewonski and Anderson, PEPI, 1981

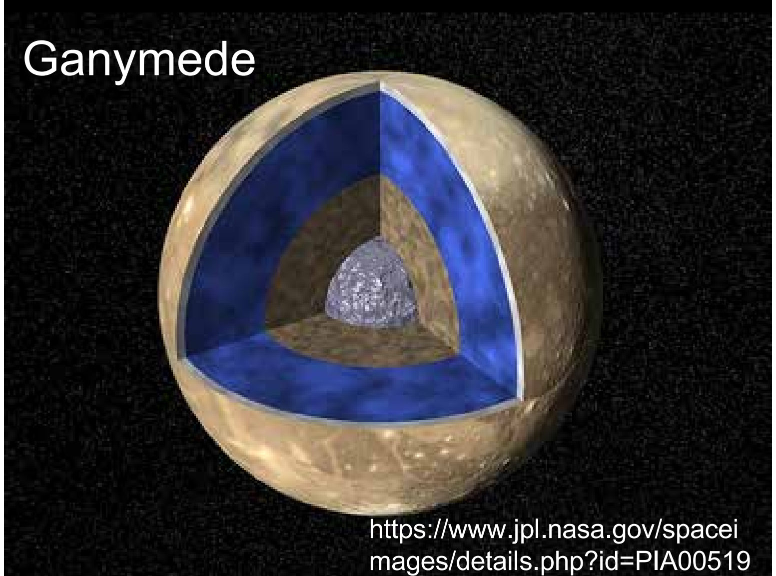
Molten Fe cores in other planetary bodies



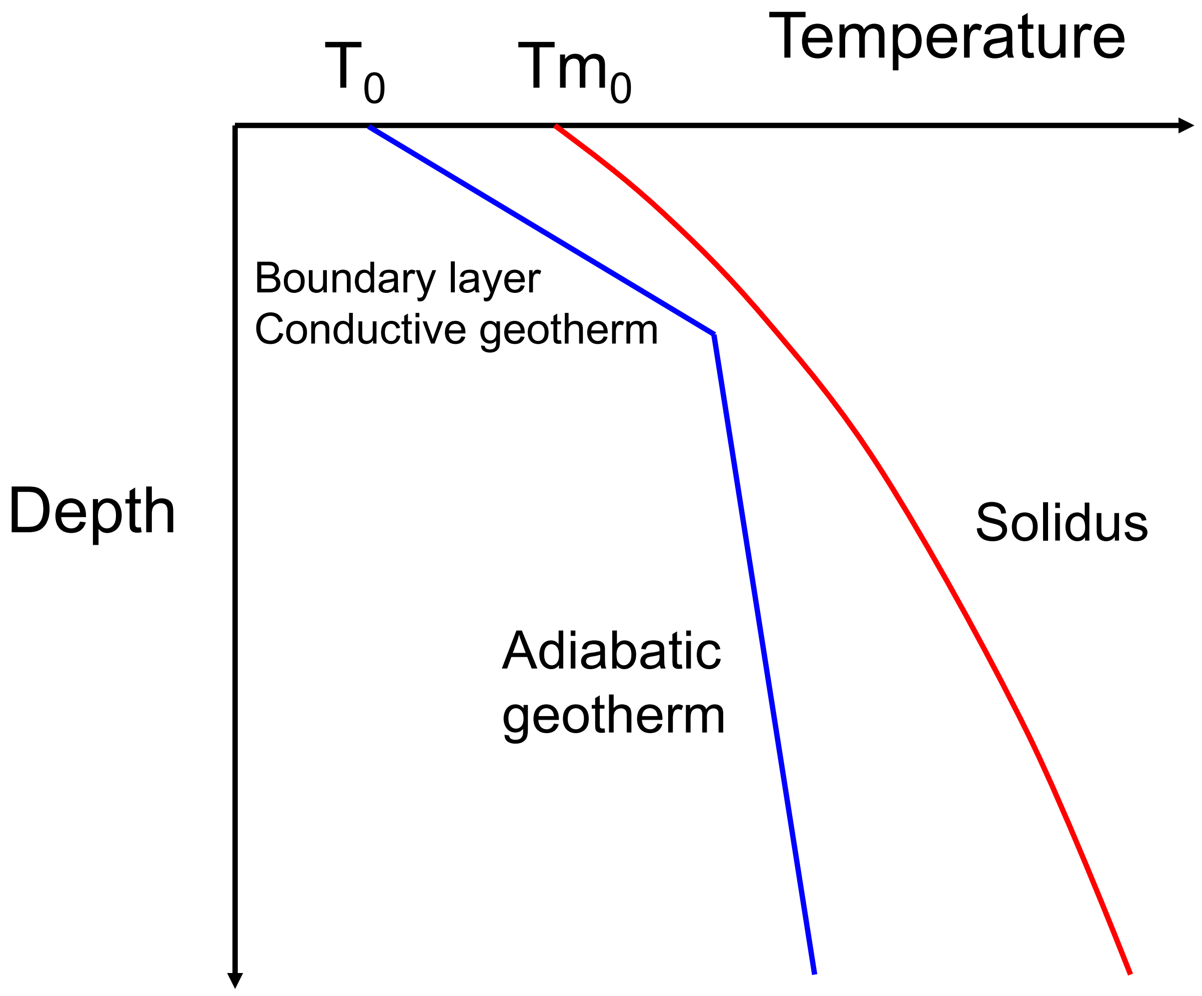
Moon



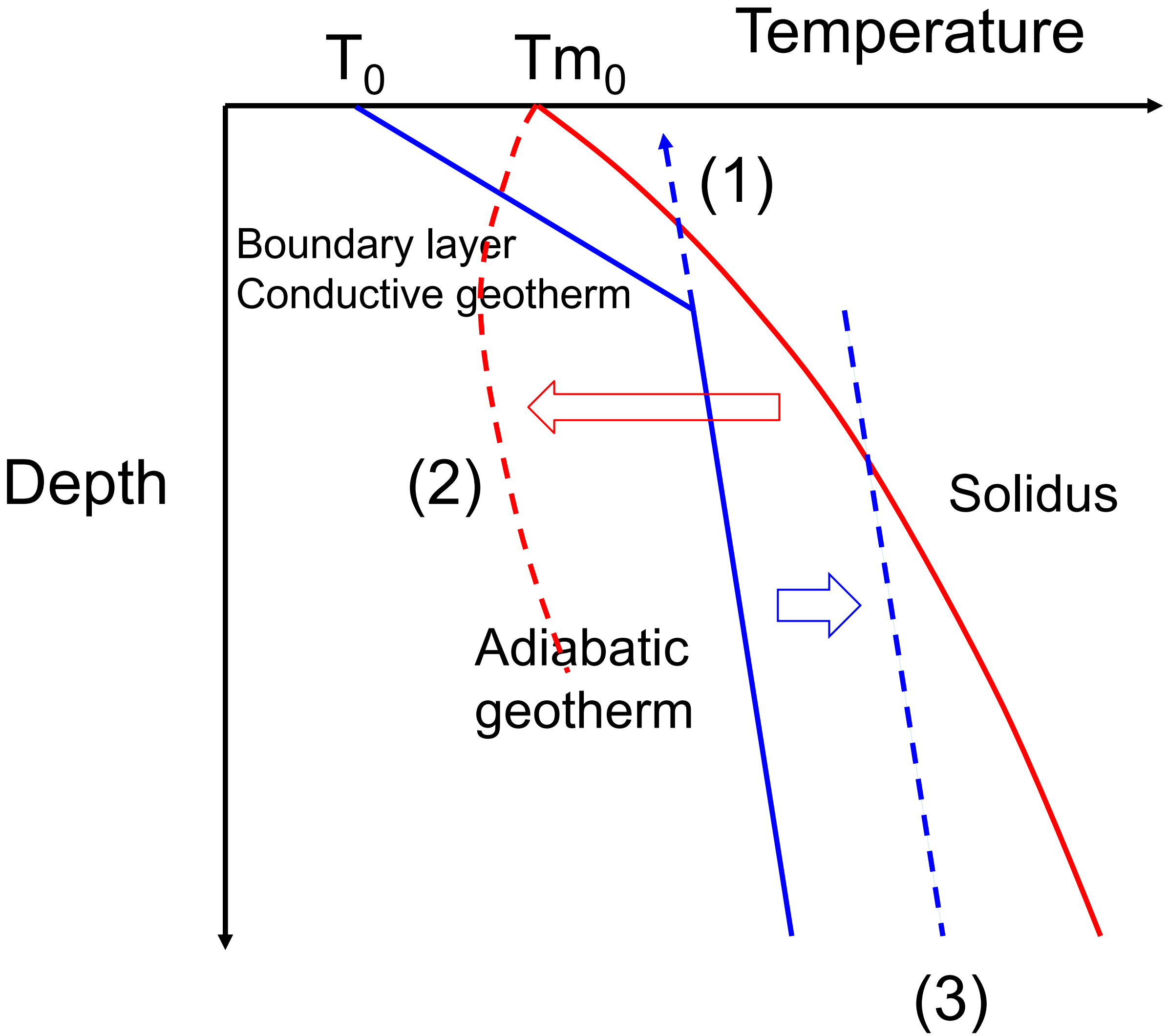
Weber et al., 2011



No melting under normal mantle conditions

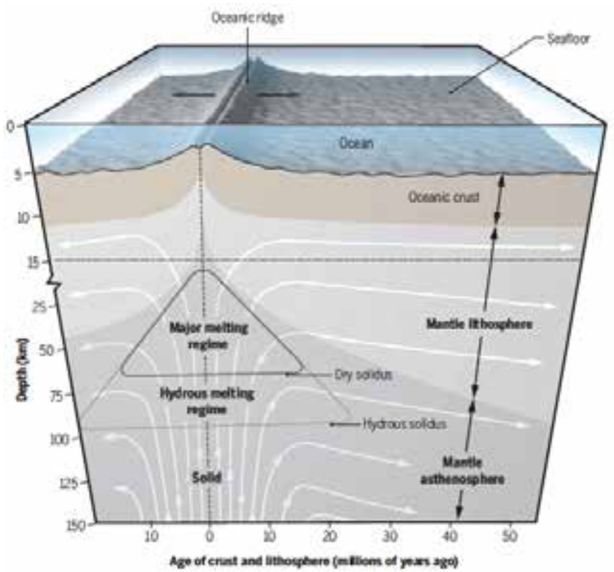


Mechanisms of mantle melting

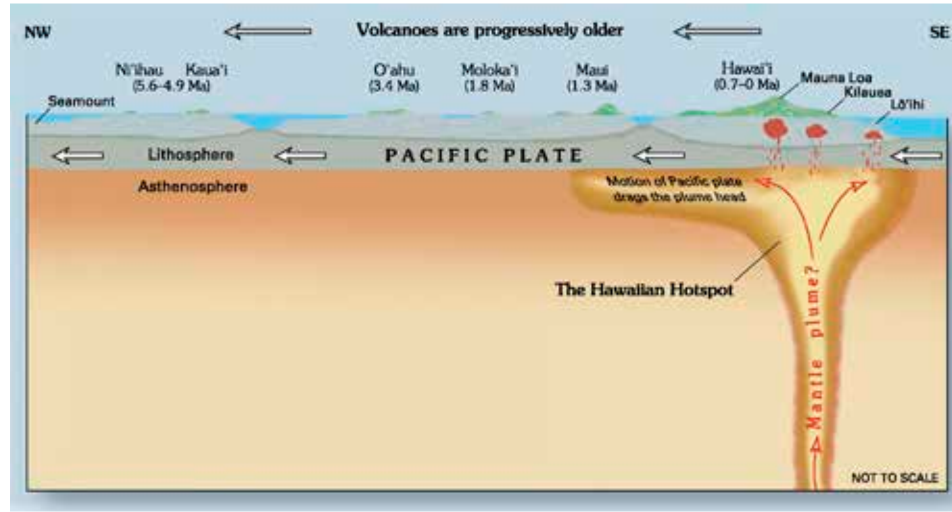


(1) Decompression melting
(2) Hydration melting
(3) Melting by increasing temperature

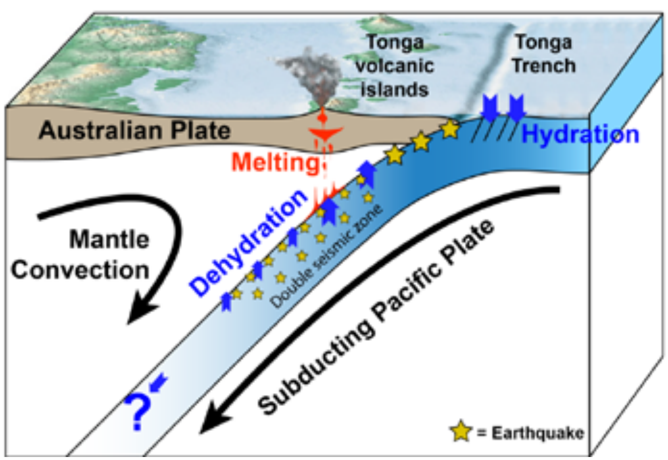
Examples of mantle melting



Asimow, 2017



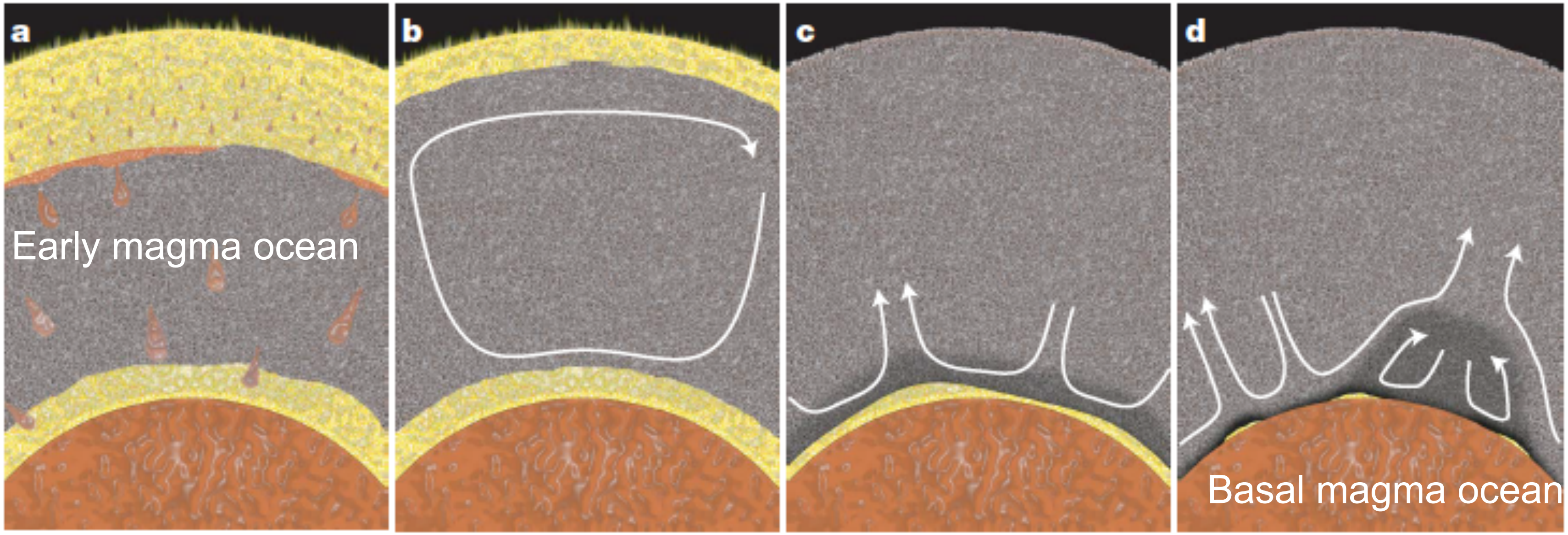
Simkin et al., 2006



Credit: S. Shawn Wei

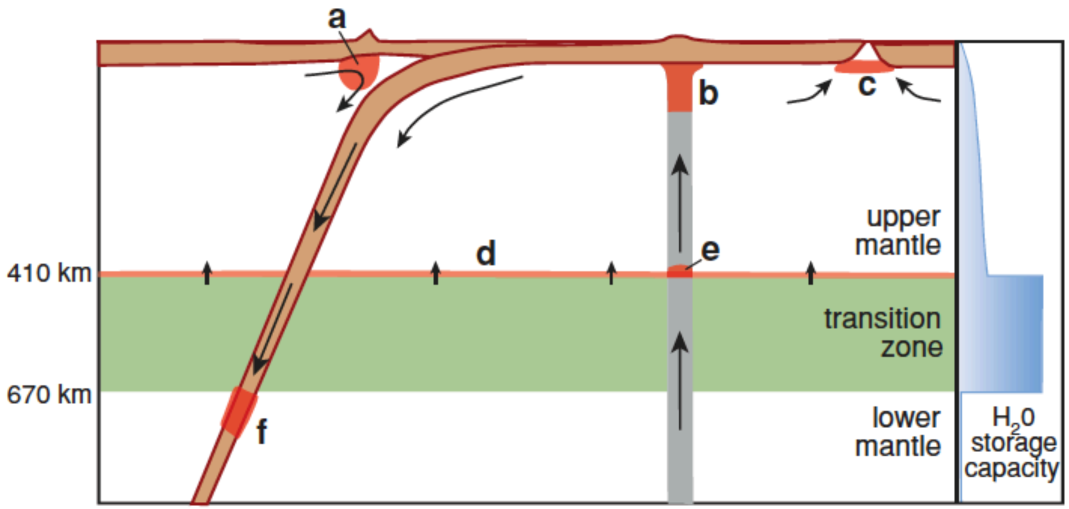
Melting at mid-ocean ridges, ocean islands, and subduction zones:
CIDER 2018 lecture by **Esteban Gazel**

Primordial melting in the mantle

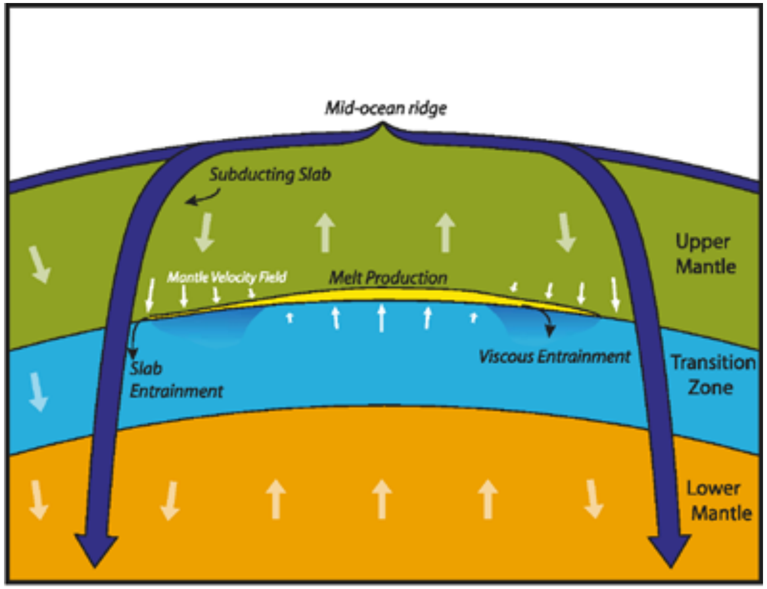


Labrosse, 2007

Volatile induced deep melting

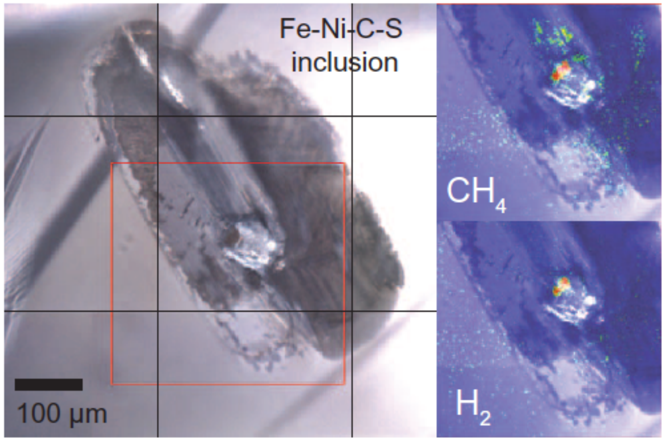


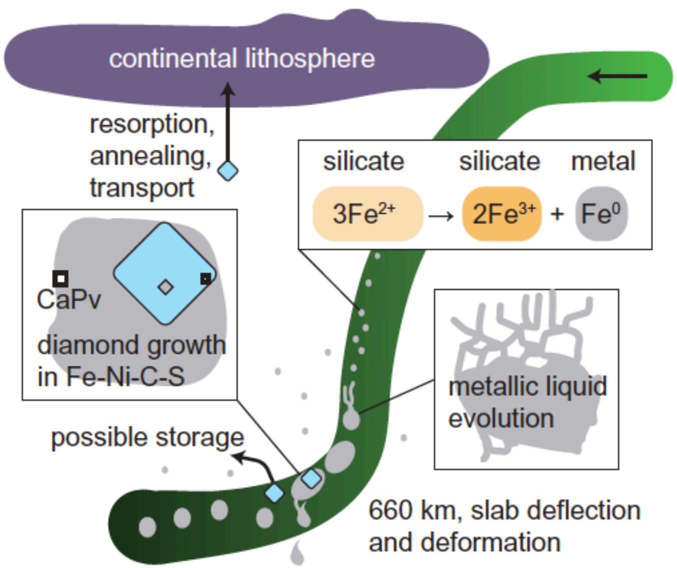
Hirschmann, 2006



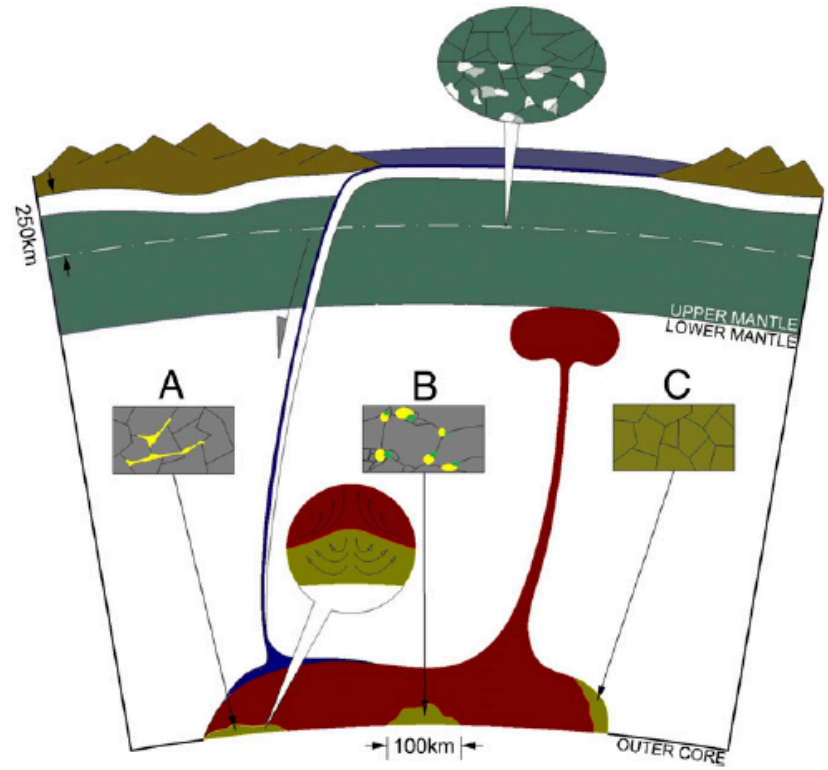
Leahy and Bercovici, 2007

Metallic melts in the deep mantle





Smith et al, 2016



Liu et al., 2016

Why do we care about melts and melting (or solidification)?

- Understanding the chemical evolution of Earth
  - Core formation
  - Formation of crusts
  - Distribution of heat producing elements
  - Cycling of volatiles
- Understanding composition and heterogeneities of the deep Earth
  - Composition of the outer core
  - Stability of melts in the deep mantle
  - Interpretation of seismic velocity anomalies, attenuation, and anisotropy
- Understanding the cooling of Earth
  - Magma ocean solidification
  - Solidification of the outer core and the generation of the intrinsic magnetic field

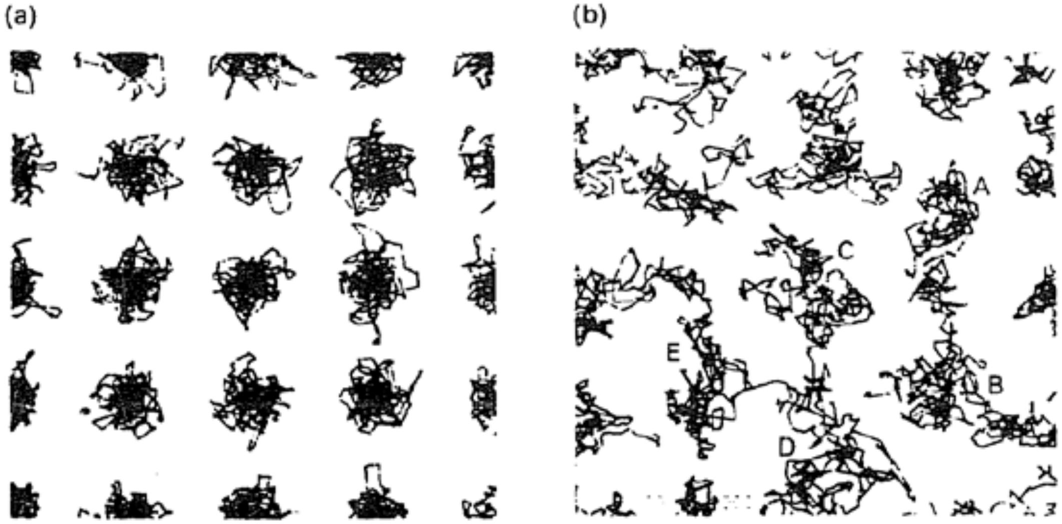
Past CIDER lectures related to melting and melts:

2010 **Cin-Ty Lee**, Melting of mantle
2011 **David Kohlstedt**, Melt and rheology
2013 **Rajdeep Dasgupta**, Melting in ridges, subduction zones
2014 **Paul Asimow**, Melting in planetary interiors
2015 **Marc Hirschmann**, Melting, deep Earth water and carbon
2016 **Frank Spera**, Thermodynamics of melting
2018 lectures by **Esteban Gazel**, **Lars Stixrude**, **Chrystele Sanloup**

This lecture will cover:

1. Physics of melting
2. Equations of state of melts
3. Solidification of melts

What is melting?



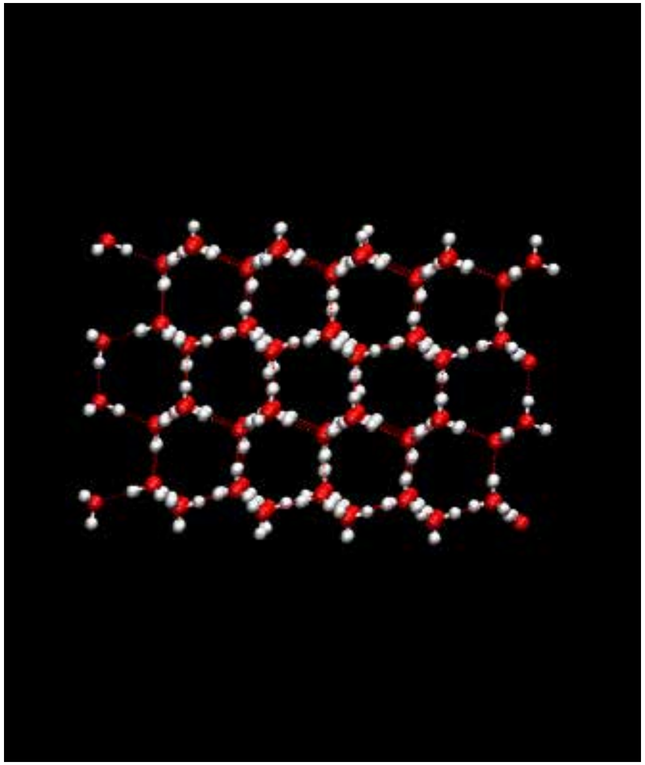
Tabor, 1991

Solid
Crystalline lattice
Periodically ordered

Liquid
Short range order
No long range order

Melting

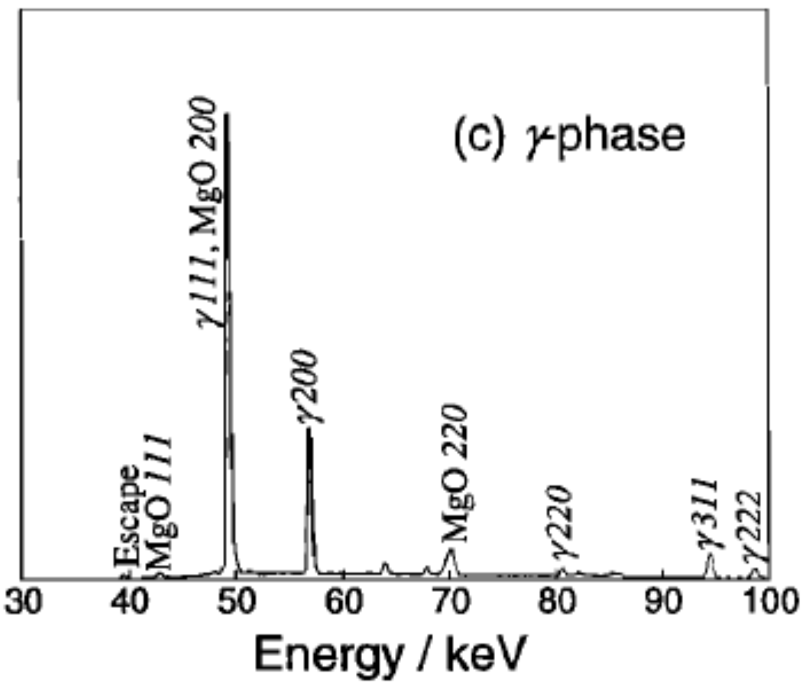
Ice melting



http://www.nyu.edu/classes/tuckerman/pchem/extras/extras.html

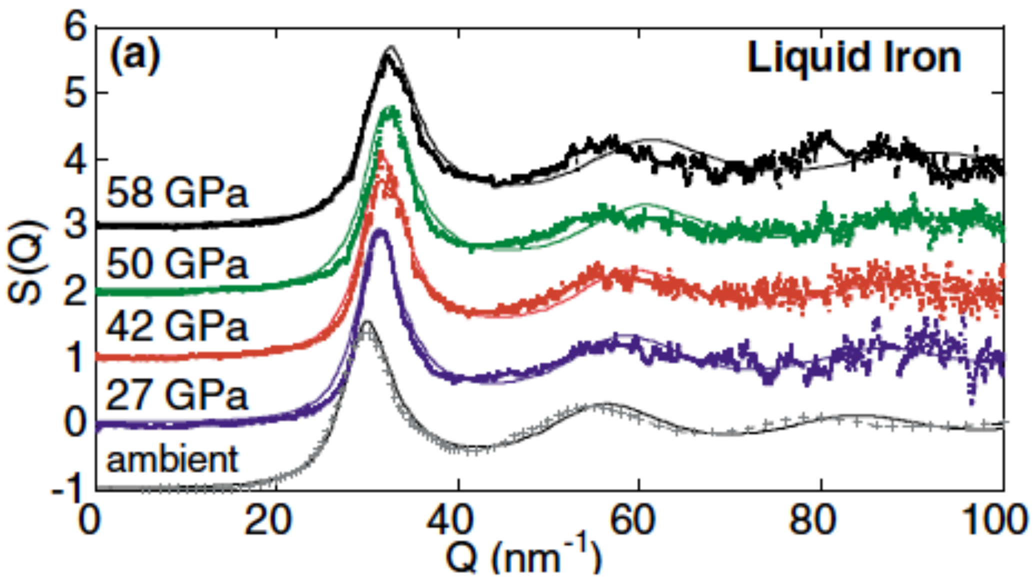
Structure of liquids from X-ray diffraction

fcc-Fe



Uchida et al, 2001

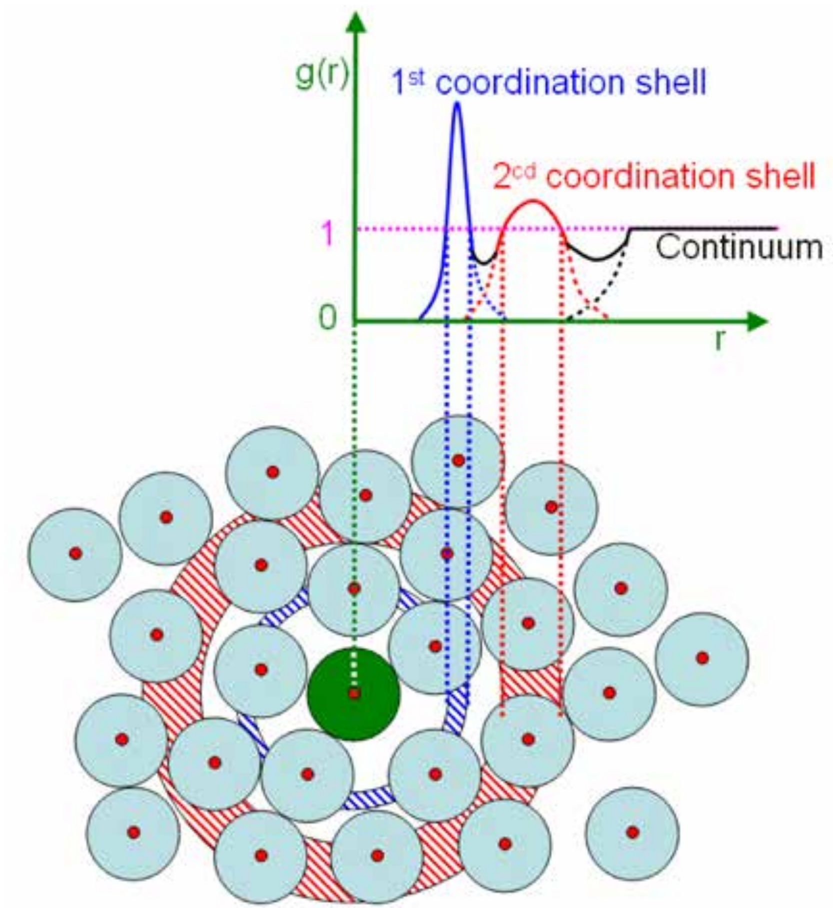
Liquid Fe



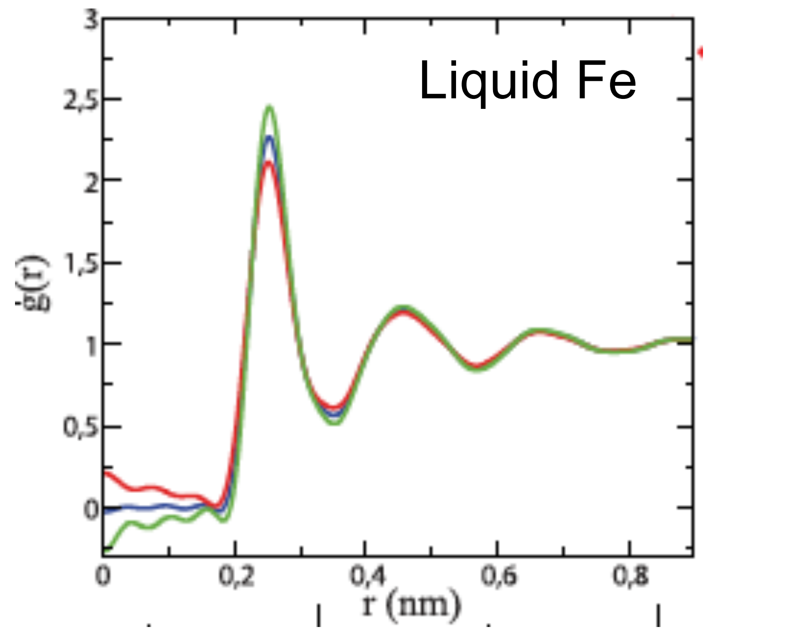
Shen et al., 2004

Short range order in liquids

Pair distribution function

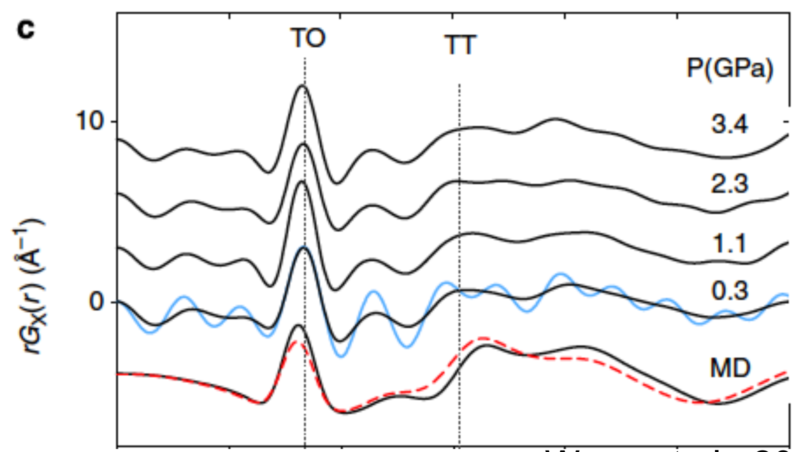


http://www.globalsino.com/EM/page3097.html



Morard et al., 2014

Liquid Di ($CaMgSi_2O_6$)



Wang et al., 2014

Theories of melting

1. Melting theories based on the thermodynamic condition that the free energies of solids and liquids are equal.

    Clausius-Clapeyron relation

2. Melting theories based on the stability of solids near its melting point.

    Lindemann's law of melting

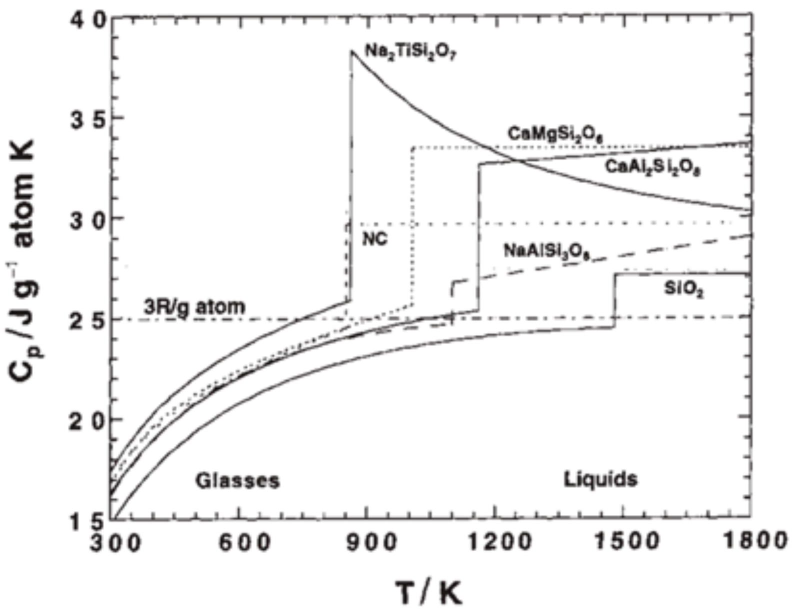
3. Empirical relations

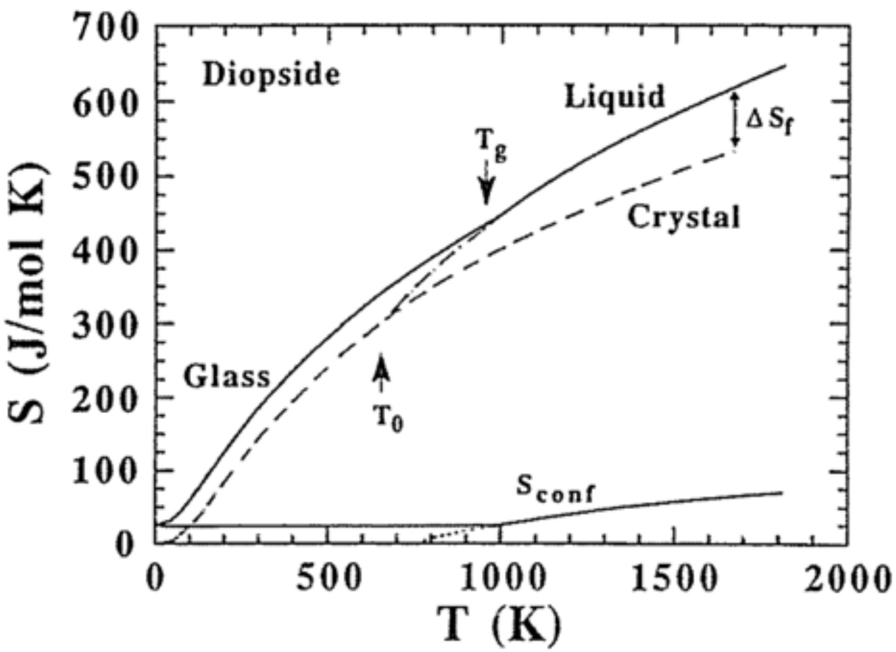
    Simon-Glatzel equation

    Kraut-Kennedy equation

Heat capacity and entropy of liquids

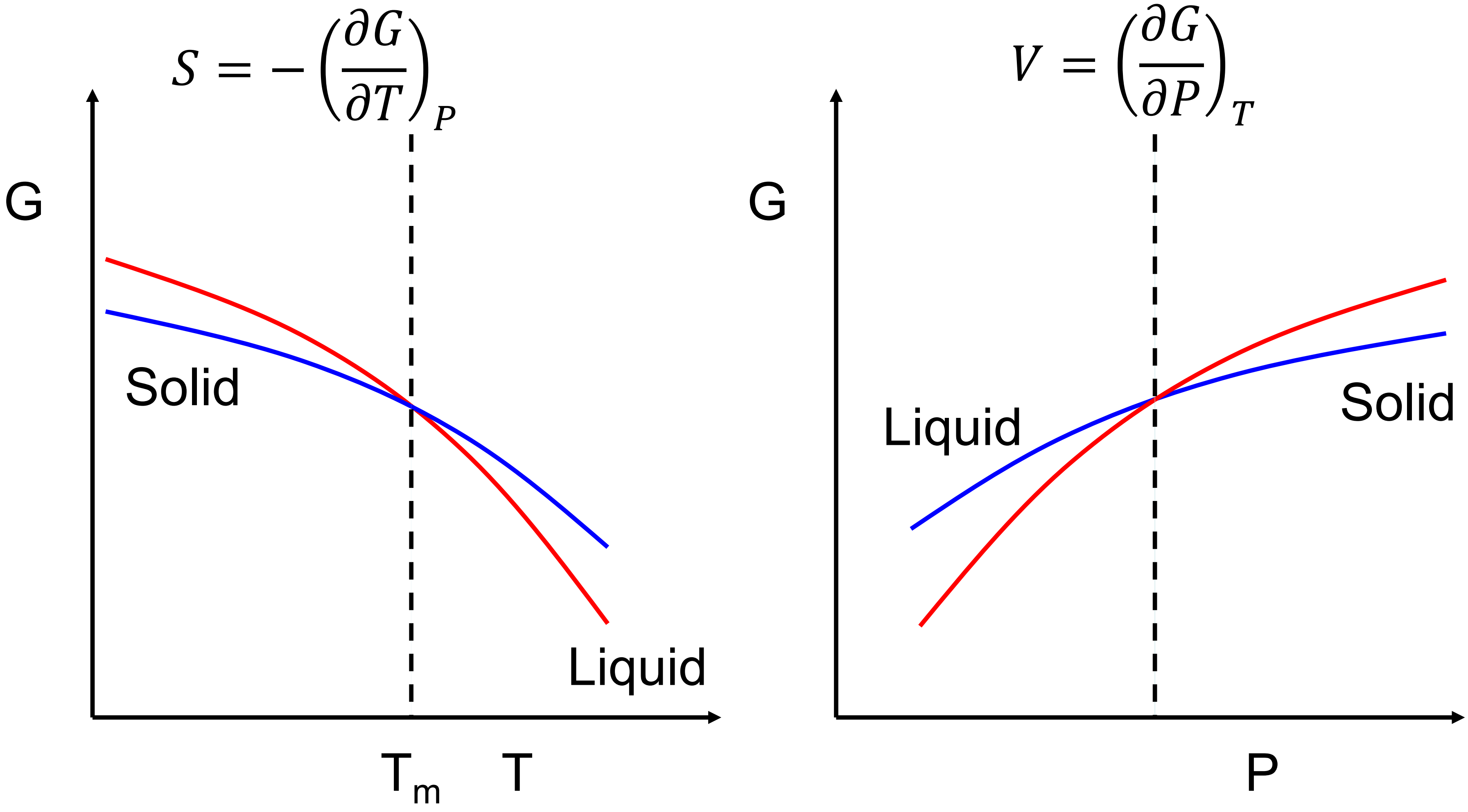
- $C_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P \qquad S = \int_0^T \frac{C_P}{T'}\,dT'$
- Crystals and glasses have similar C_p. However, liquids have higher C_p and entropy due to additional degrees of freedom, i.e., the freedom of having different spatial configurations.





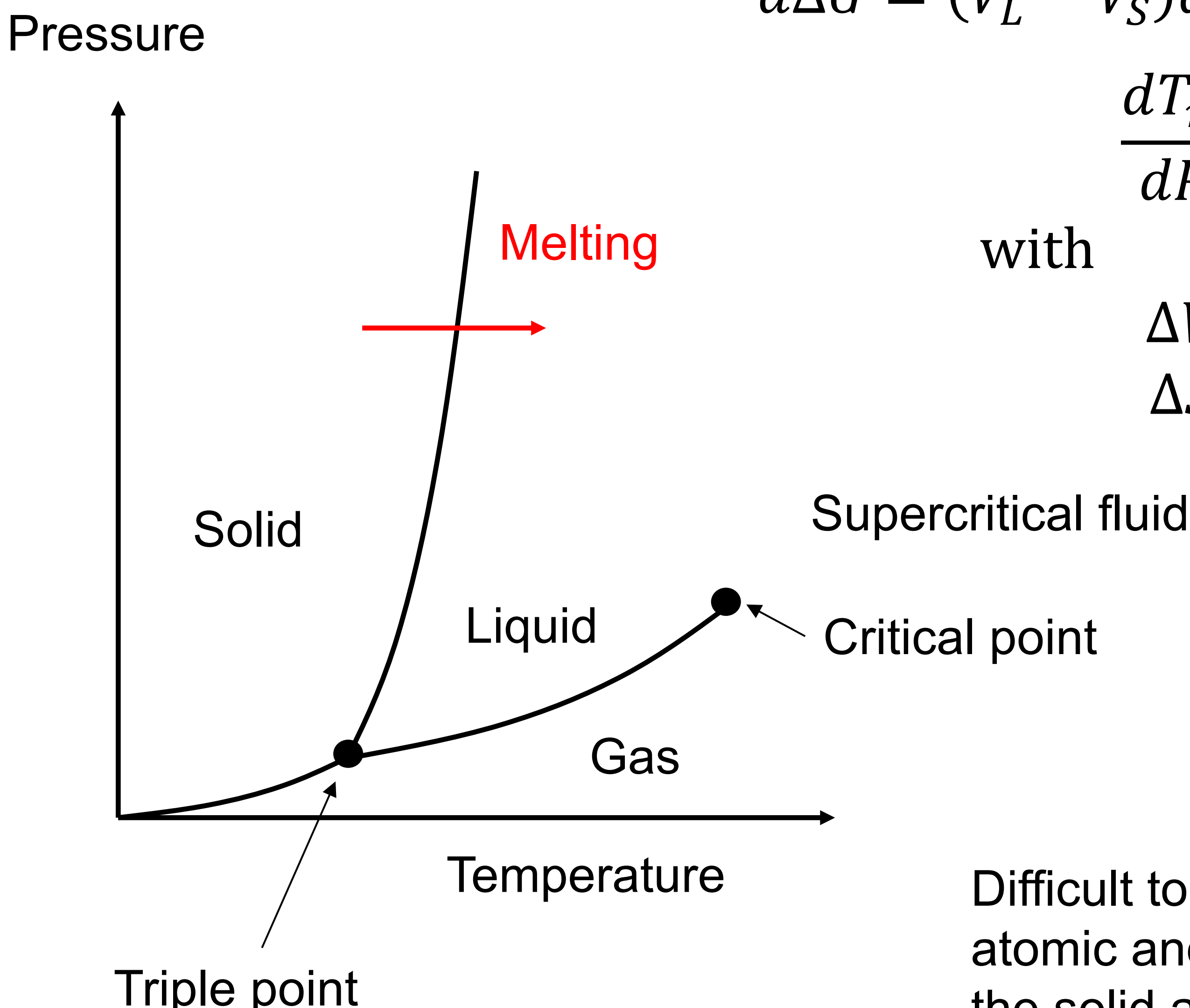
Richet & Neuville, 1992

One component system: Gibbs free energy



Melting is a first order phase transition. The first order derivatives of G are discontinuous across the transition.

Clausius-Clapeyron relation



$$d\Delta G = (V_L - V_S)dP - (S_L - S_S)dT = 0$$

$$\frac{dT_m}{dP} = \frac{\Delta V_m}{\Delta S_m}$$

with

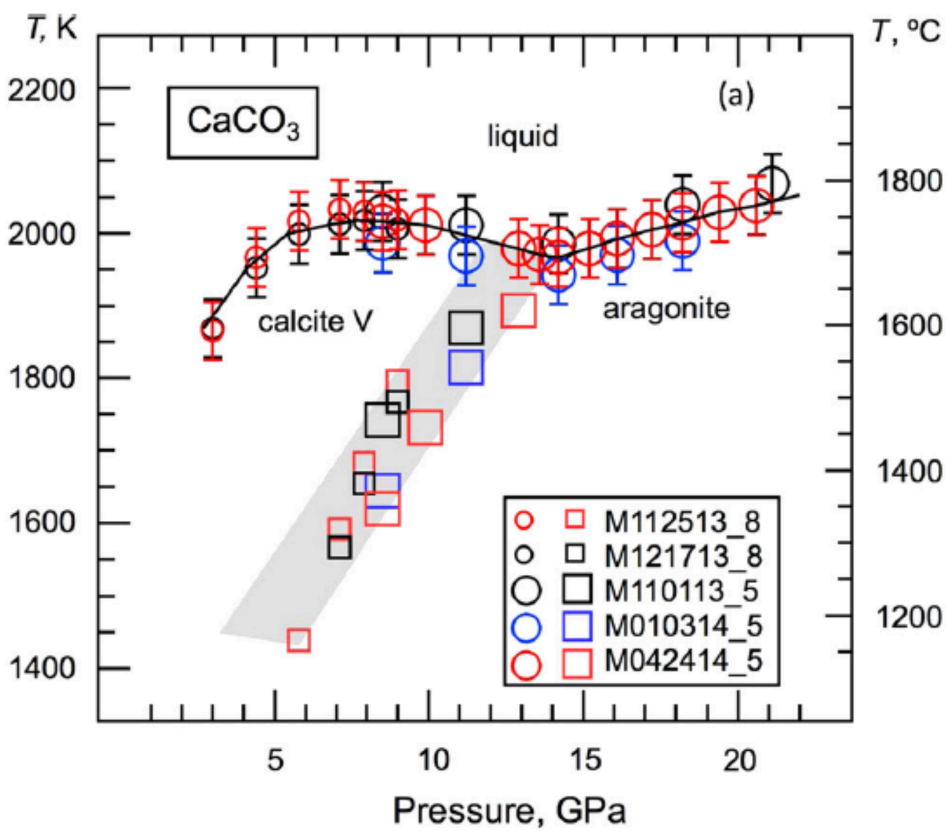
$$\Delta V_m = V_L - V_S$$
$$\Delta S_m = S_L - S_S$$

Difficult to quantify the detailed atomic and electronic structures of the solid and liquid (Tallon, 1982)

Negative volume of melting

$$\frac{dT_m}{dP} = \frac{\Delta V_m}{\Delta S_m}$$

ΔS is always larger than 0. A negative slope in the melting curve indicates the liquid is denser than the solid.



Li et al., 2017

Lindemann's law of melting

- Melting occurs when the vibration of atoms is at a critical fraction *f* of the distance r_0 of nearest neighbors.

$$< a^2 > = f^2 r_0^2$$

- From Debye's approximation,

$$< a^2 > \cong \frac{9 k_B T}{m \omega_D^2} = \frac{9 \hbar^2 T}{m k_B \theta^2}$$

where $\theta = \frac{\hbar \omega_D}{k_B}$ is Debye temperature

- Lindemann's law

$$T_m = f^2 \frac{k_B}{9 \hbar^2} m \theta^2 v^{\frac{2}{3}}$$

m – mean atomic mass
v – mean atomic volume

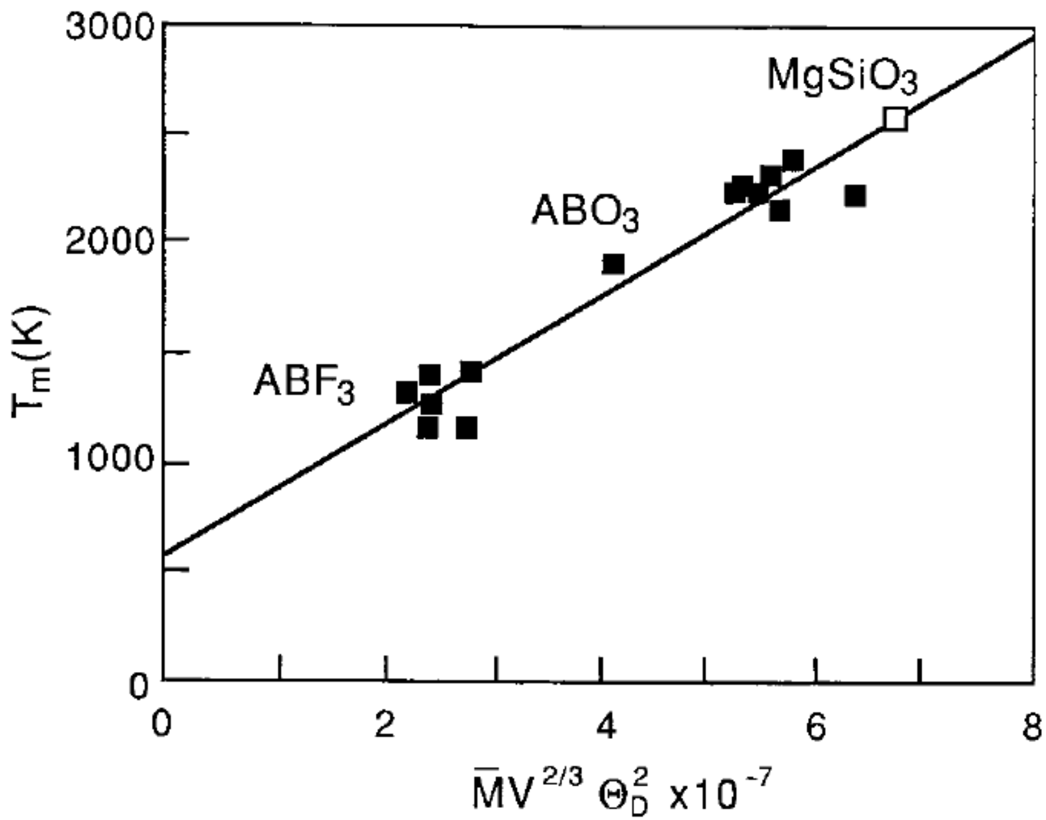
- Differential form

$$\frac{d \ln T_m}{d \ln \rho} = 2\left(\gamma - \frac{1}{3}\right)$$

where $\gamma = \frac{d \ln \omega}{d \ln \rho} = \frac{d \ln \theta}{d \ln \rho}$

Lindemann factor *f*

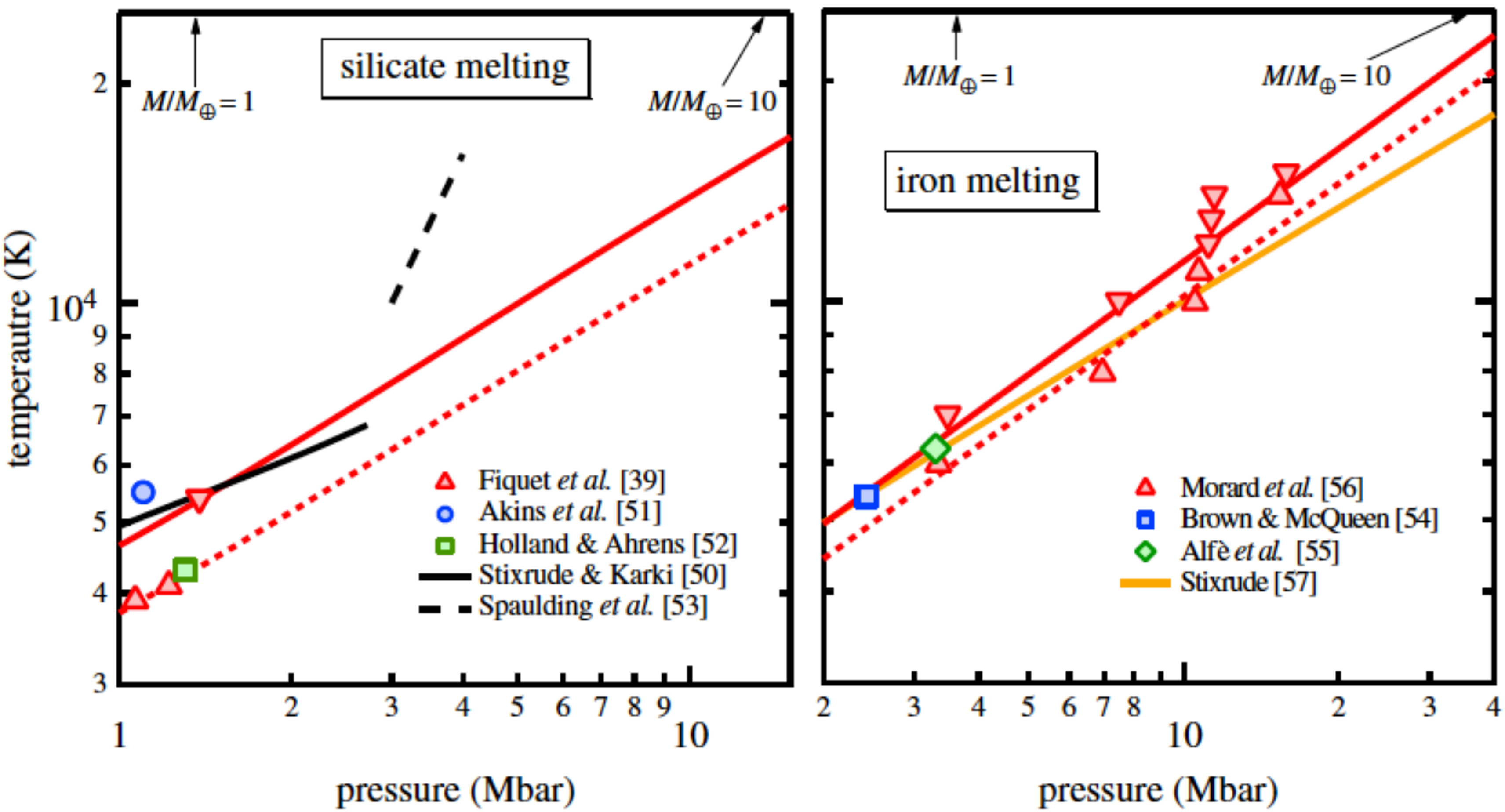
- The Lindemann's melting law is supported by the observations that for many metals *f* is about 0.08, and for perovskite oxides *f* is about 0.13.



Poirier, 1989

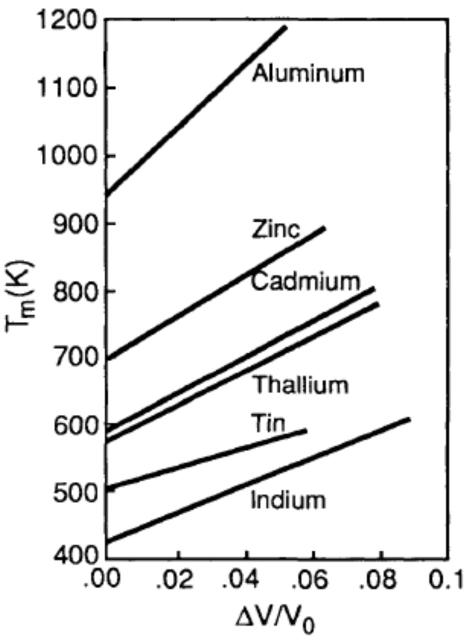
Melting in super-earths: extrapolation using Lindemann's law

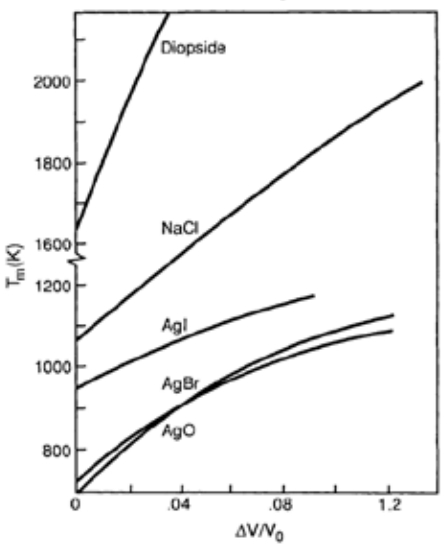
f = 0.137 for $MgSiO_3$ post-perovskite



Stixrude, 2014

Kraut-Kennedy equation





Kennedy and Vaidya, 1970

Approximate Lindemann's law

$$\frac{d\ln T_m}{d\ln\rho} = 2\left(\gamma - \frac{1}{3}\right)$$

with a finite difference equation

$$\frac{\Delta T_m}{T_m} = \frac{T_m - T_{m0}}{T_m} = 2\left(\gamma - \frac{1}{3}\right)\frac{\Delta V}{V_0}$$

That is

$$T_m = T_{m0}\left[1 + 2\left(\gamma - \frac{1}{3}\right)\frac{\Delta V}{V}\right]$$

Kraut-Kennedy equation (Kraut and Kennedy, 1966)

$$T_m = T_{mo}\left(1 + C\frac{\Delta V}{V}\right)$$

Generally cannot be used at very high pressures.

Simon-Glatzel equation

Combine Lindemann's law and Murnaghan EOS

$$\frac{d \ln T_m}{d \ln \rho} = 2\left(\gamma - \frac{1}{3}\right)$$

and

$$K_T = K_{T0} + K'_{T0} P$$

where $K_T = \left(\frac{\partial P}{\partial \ln \rho}\right)_T$, we have

$$T_m = T_{m0}\left[1 + K'_{T0}\left(\frac{P}{K_{T0}}\right)\right]^{2\left(\gamma - \frac{1}{3}\right)}$$

Simon's law (Simon and Glatzel, 1929)

$$T_m = T_{mo}\left(1 + \frac{P}{a}\right)^b$$

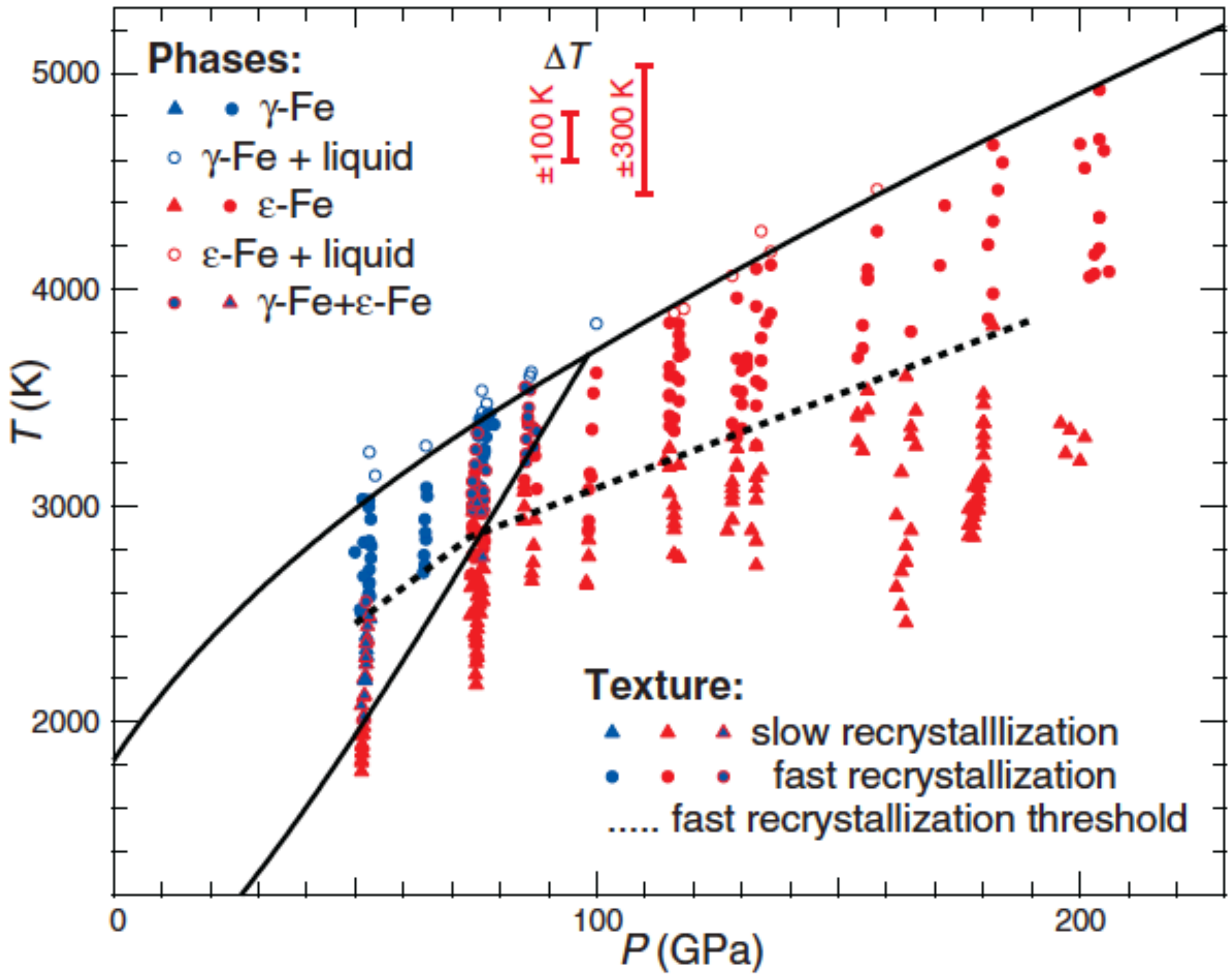
or

$$\frac{P - P_0}{a} = \left(\frac{T_m}{T_0}\right)^c - 1$$

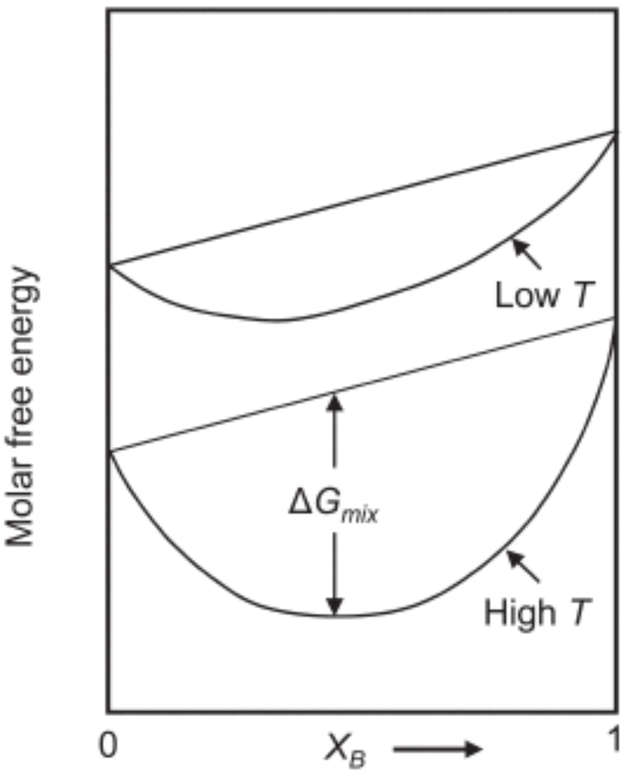
Melting curve of Fe fitted by Simon-Glatzel equation

Anzellini et al. (2013):

$$(P - P_0)/27.39 = (T_m/T_0)^{2.38} - 1$$
$$(\gamma - \mathrm{Fe/liquid})$$
$$(P - P_{TP})/161.2 = (T_m/T_{TP})^{1.72} - 1$$
$$(\varepsilon - \mathrm{Fe/liquid})$$



Gibbs free energy of binary ideal solutions



Porter and Esterling, 1981, Phase transformations in metals and alloys

For ideal solution of two components A and B,

$$G = X_A G_A + X_B G_B - T\Delta S_{mix}$$

where

$$\Delta S_{mix} = -k_B \ln \Omega = -k_B \ln \frac{(N_A + N_B)!}{N_A!\, N_B!}$$
$$= -R(X_A \ln X_A + X_B \ln X_B)$$

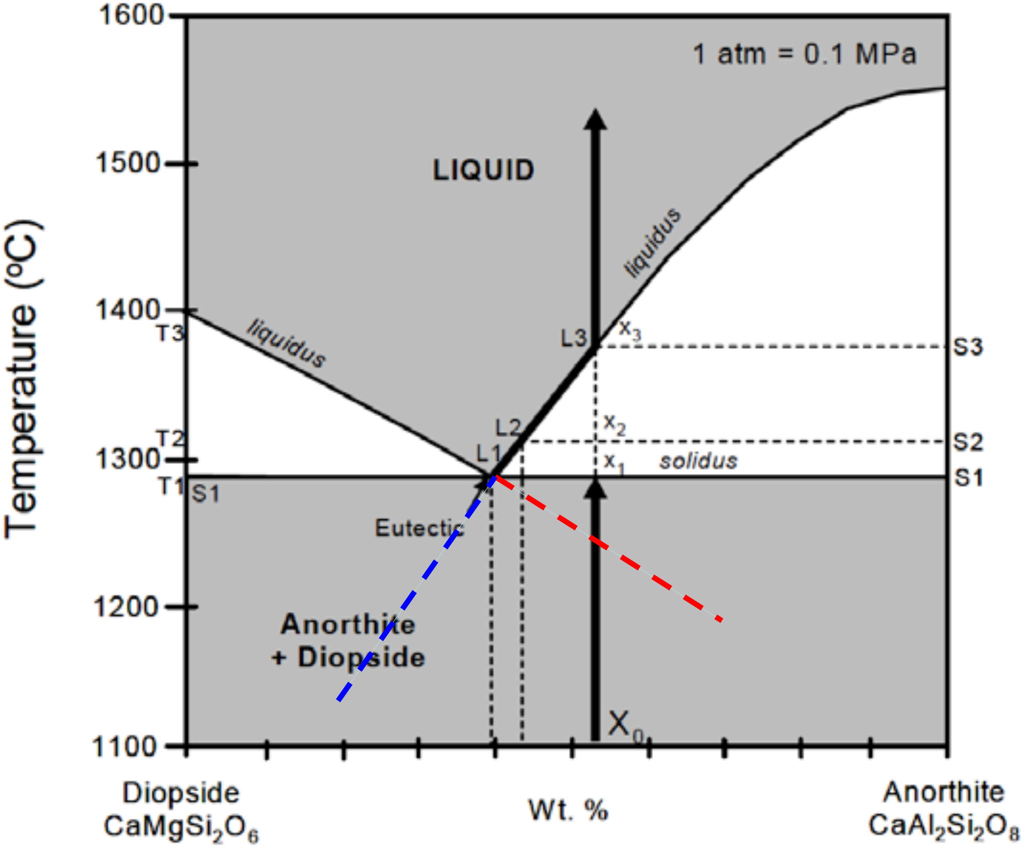
Compare to the Euler form

$$G = X_A \mu_A + X_B \mu_B$$

We get

$$\mu_A = \mu_A^0 + RT \ln X_A$$
$$\mu_B = \mu_B^0 + RT \ln X_B$$

Melting in the binary systems – Eutectic melting



Bowen, 1915

$$\mu_{Di}^{s} = \mu_{Di}^{s0}$$
$$\mu_{Di}^{l} = \mu_{Di}^{l0} + RT\ln X_{Di}^{l}$$

During melting

$$\mu_{Di}^{s0} = \mu_{Di}^{l0} + RT\ln X_{Di}^{l}$$

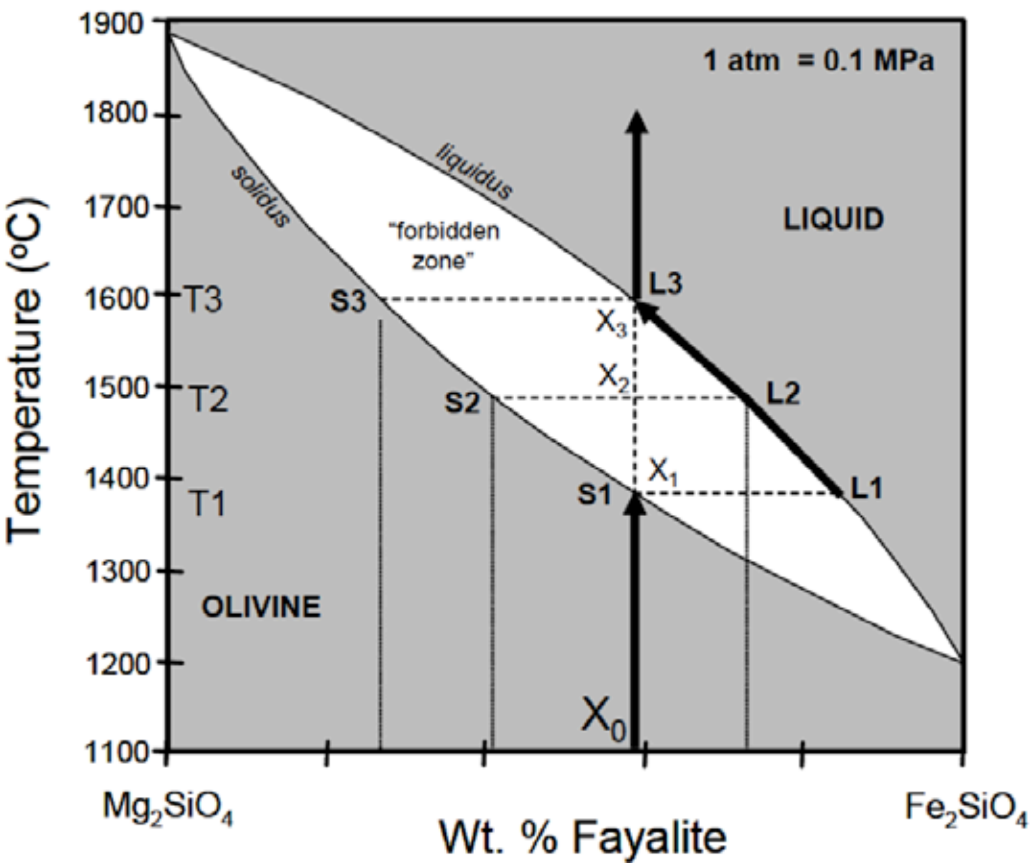
Liquidus curve

$$\ln X_{Di}^{l} = \frac{1}{RT}\left(\mu_{Di}^{s0} - \mu_{Di}^{l0}\right)$$
$$= -\frac{1}{\mathrm{RT}}\Delta G_{m}^{Di} = \frac{\Delta H_{m}^{Di}}{R}\left(\frac{1}{T_{m}^{Di}} - \frac{1}{T}\right)$$

Or

$$X_{Di}^{l} = e^{-\frac{\Delta G_{m}^{Di}}{RT}}$$
$$X_{An}^{l} = e^{-\frac{\Delta G_{m}^{An}}{RT}}$$

Melting in the binary systems – Solid solution



Bowen and Chairer, 1935

$$\mu_{Fo}^{s} = \mu_{Fo}^{s0} + RT\ln X_{Fo}^{s}$$
$$\mu_{Fo}^{l} = \mu_{Fo}^{l0} + RT\ln X_{Fo}^{l}$$

During melting

$$\mu_{Fo}^{s0} + RT\ln X_{Fo}^{s} = \mu_{Fo}^{l0} + RT\ln X_{Fo}^{l}$$
$$\mu_{Fa}^{s0} + RT\ln X_{Fa}^{s} = \mu_{Fa}^{l0} + RT\ln X_{Fa}^{l}$$

Also

$$X_{Fo}^{s} + X_{Fa}^{s} = 1$$
$$X_{Fo}^{l} + X_{Fa}^{l} = 1$$

We have

$$X_{Fo}^{s} = \frac{1 - e^{-\Delta G_m^{Fa}}}{e^{-\Delta G_m^{Fo}} - e^{-\Delta G_m^{Fa}}}$$
$$X_{Fo}^{l} = \frac{e^{-\Delta G_m^{Fo}}\left(1 - e^{-\Delta G_m^{Fa}}\right)}{e^{-\Delta G_m^{Fo}} - e^{-\Delta G_m^{Fa}}}$$

with

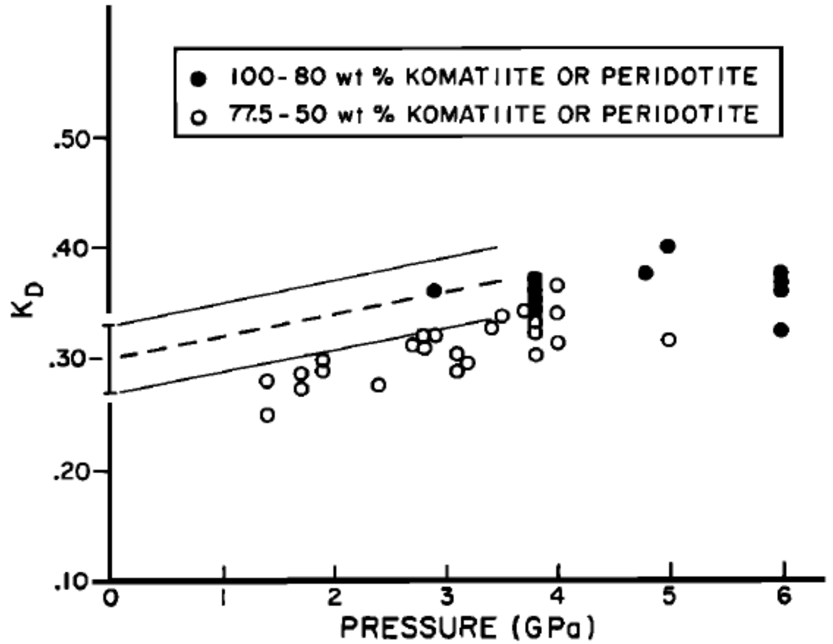
$$\Delta G_m = \Delta H_m - T\Delta S_m$$

Mg-Fe distribution between olivine and melts

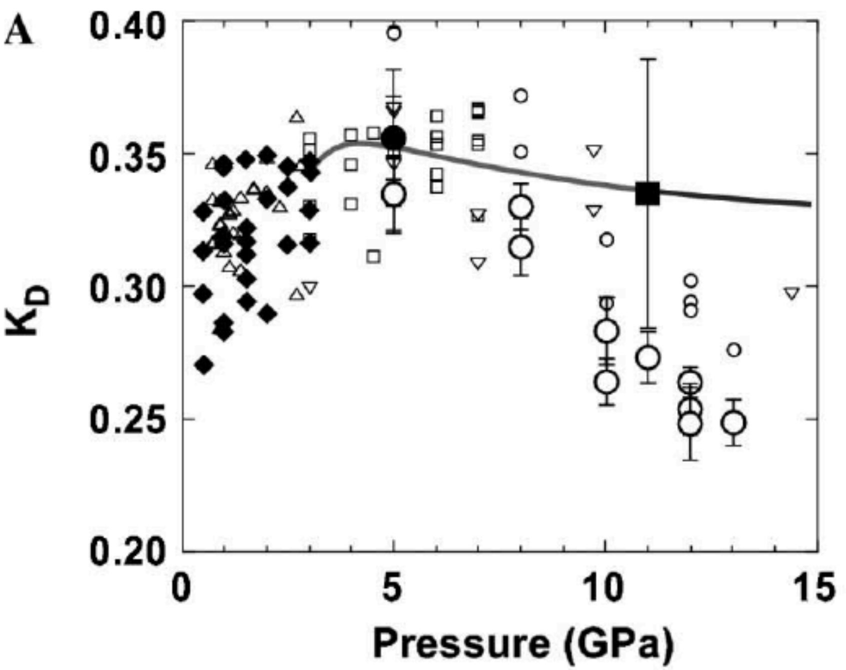
Fe-Mg distribution constant between olivine and melt is defined as

$$K_D^{Fe/Mg} = \frac{(Fe/Mg)^{ol}}{(Fe/Mg)^{melt}}$$

Smaller K_D means more Fe in the melt and the melt is denser.

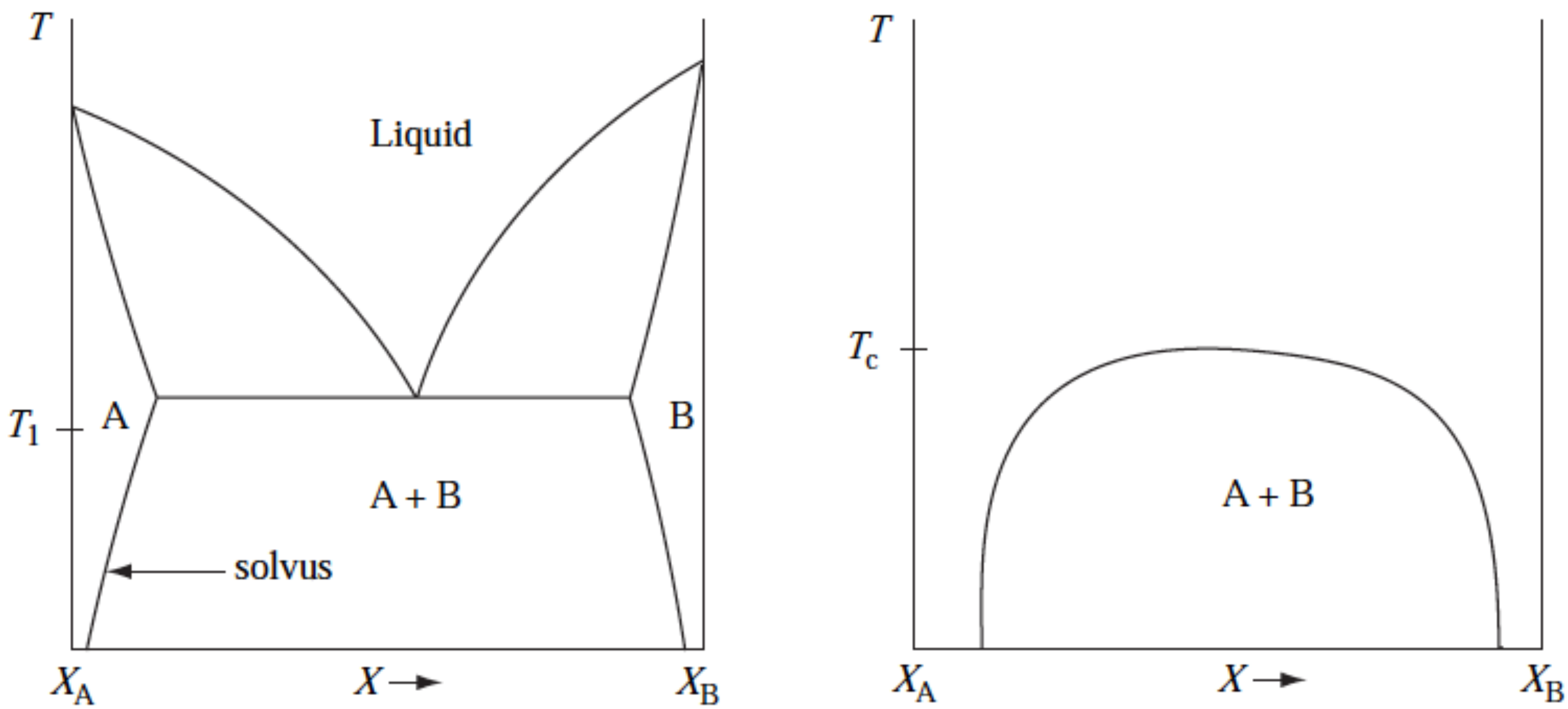


Agee and Walker, 1988



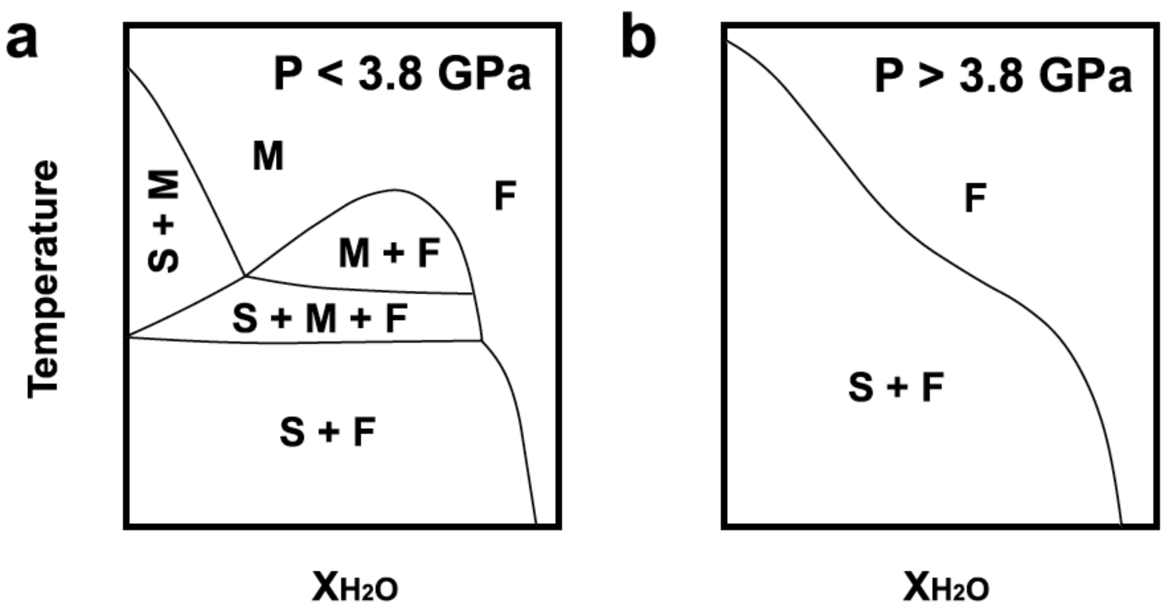
Mibe et al., 2006

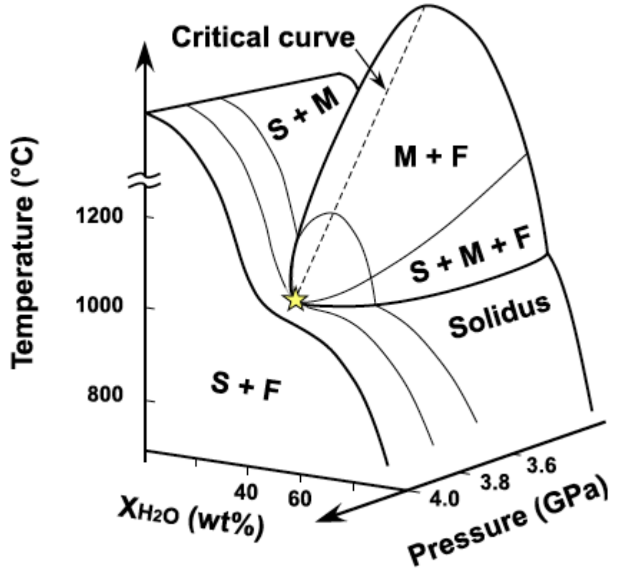
Binary phase diagram – Solvus and immiscibility

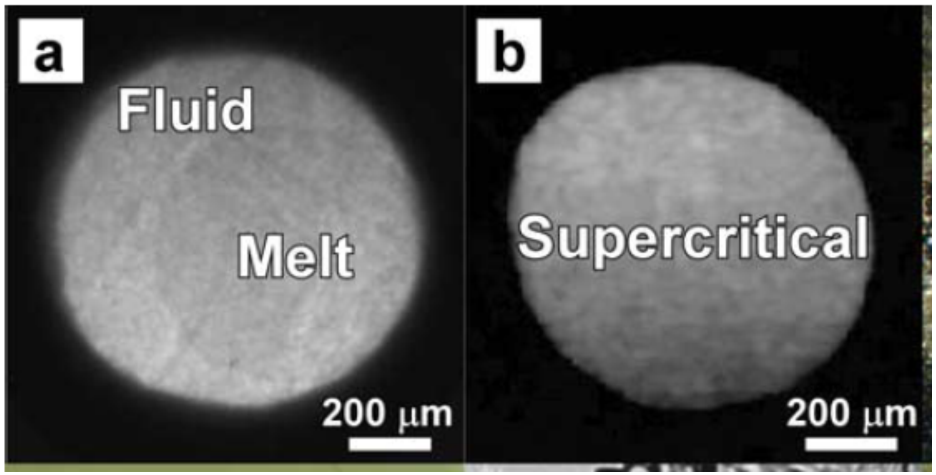


Karato, Deformation of Earth materials

Silicate – H_2O pseudo-binary phase diagrams

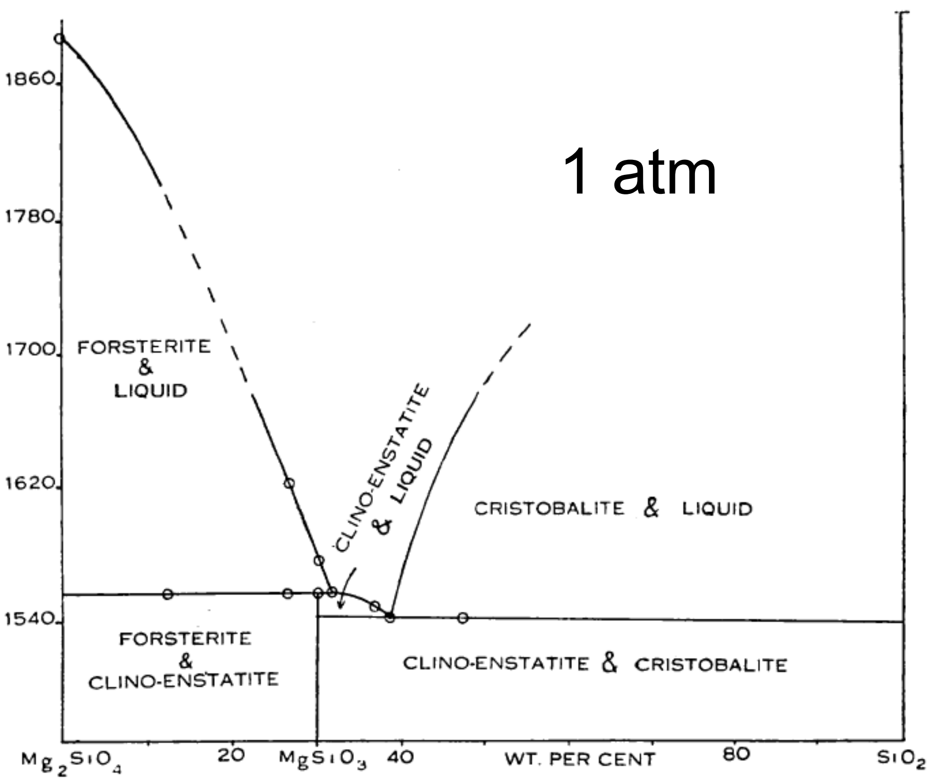




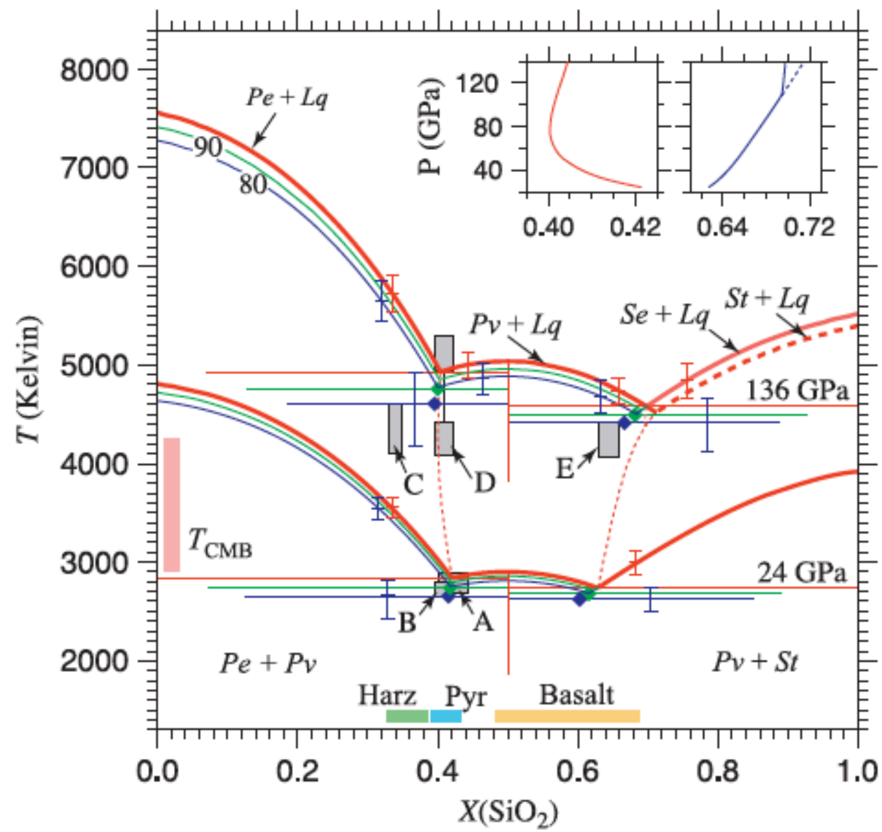


Mibe et al., 2007

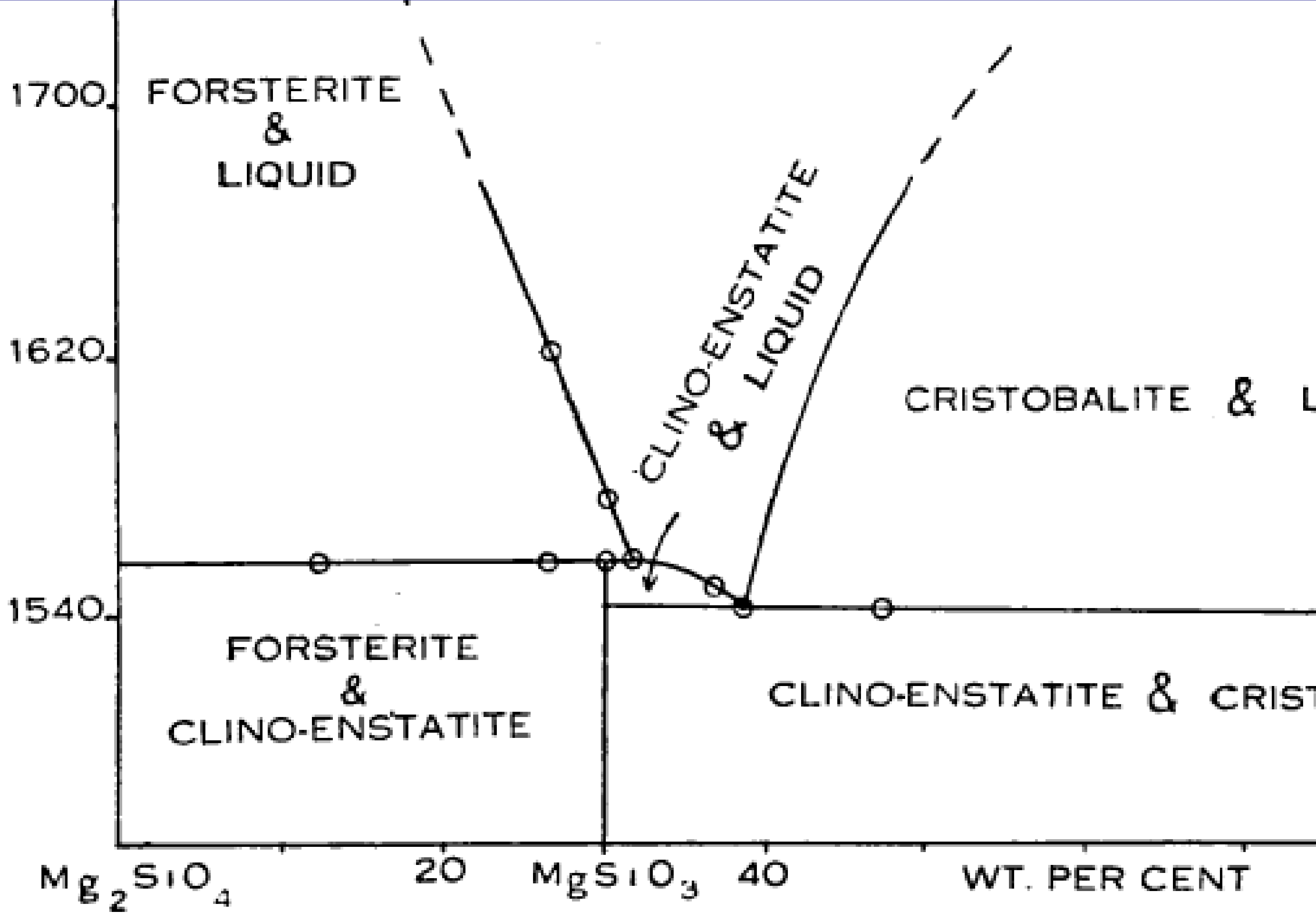
Binary phase diagram – Incongruent melting



Bowen, 1914

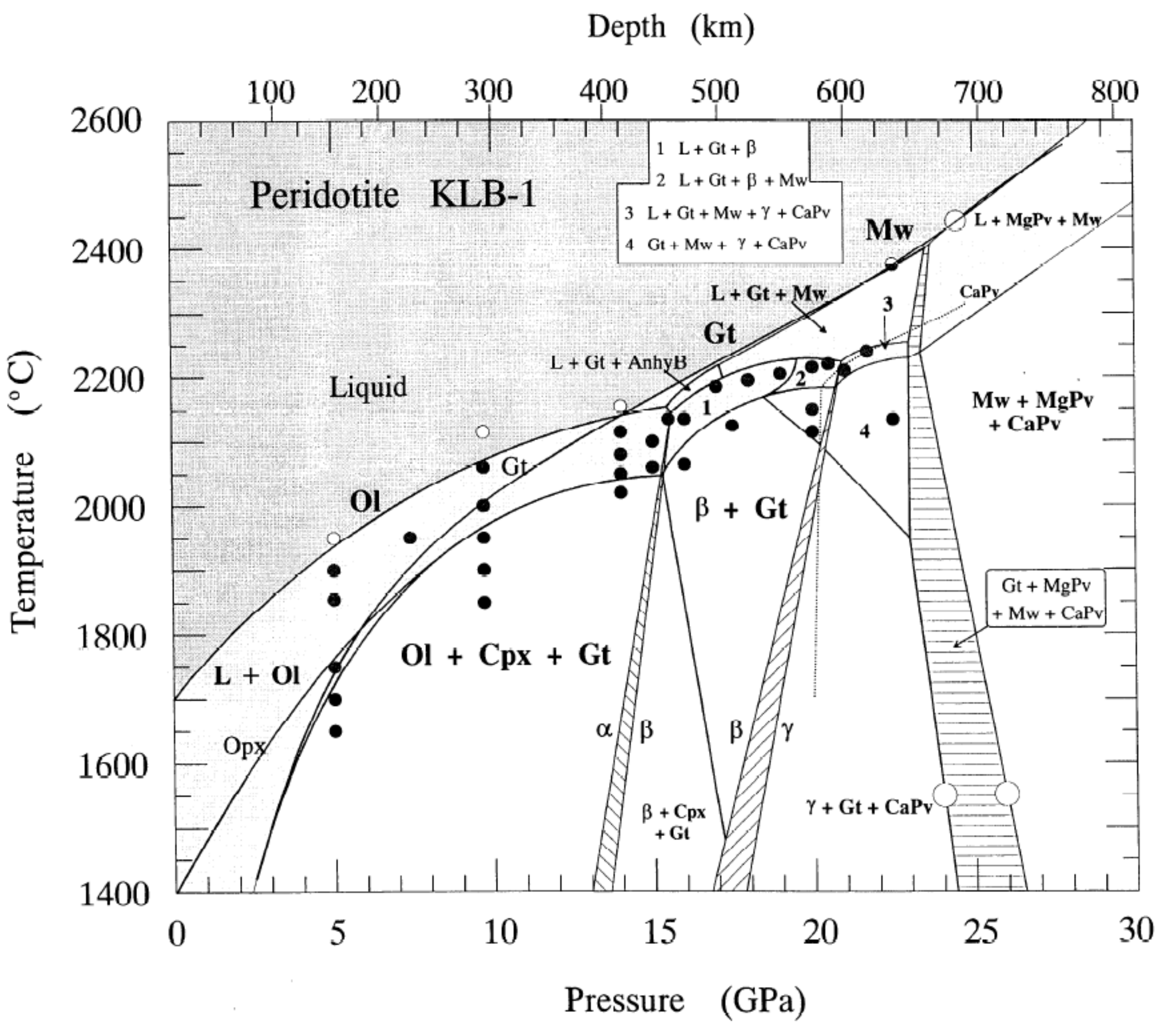


de Koker et al., 2013


1700
1620
1540
FORSTERITE
&
LIQUID
CLINO-ENSTATITE
& LIQUID
CRISTOBALITE & L
FORSTERITE
&
CLINO-ENSTATITE
CLINO-ENSTATITE & CRIST
Mg_2SiO_4
20
$MgSiO_3$
40
WT. PER CENT

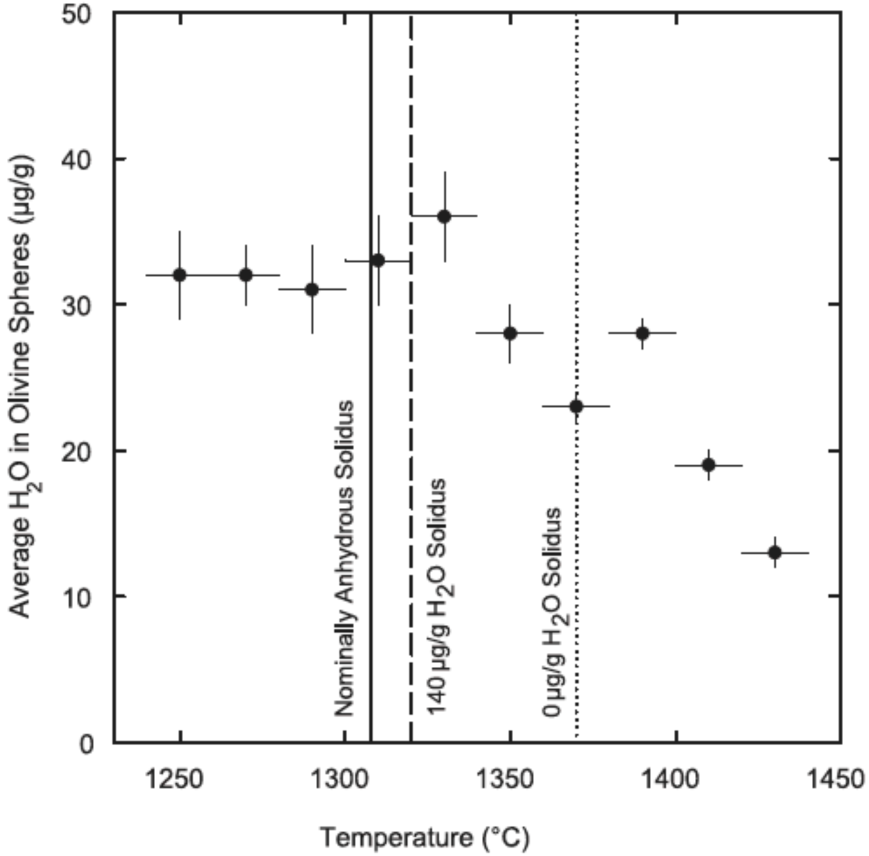
Bowen, 1914

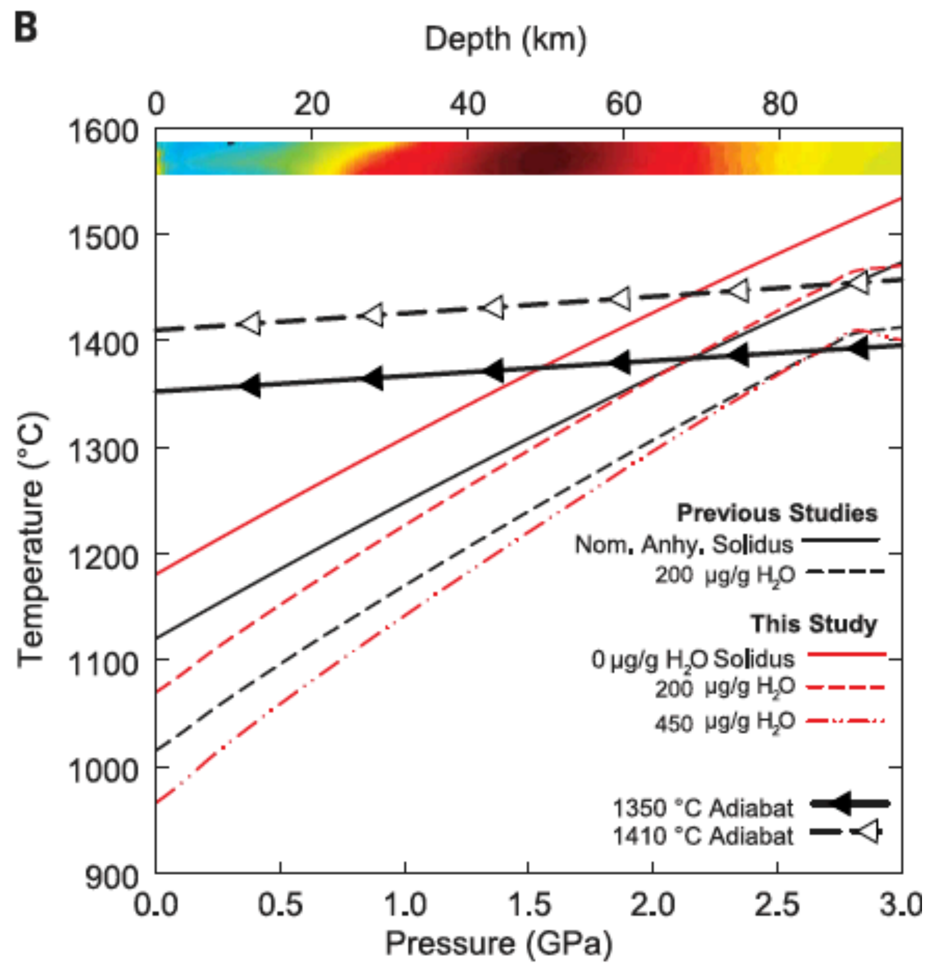
Melting relation in a multi-component system



Zhang & Herzberg, 1994

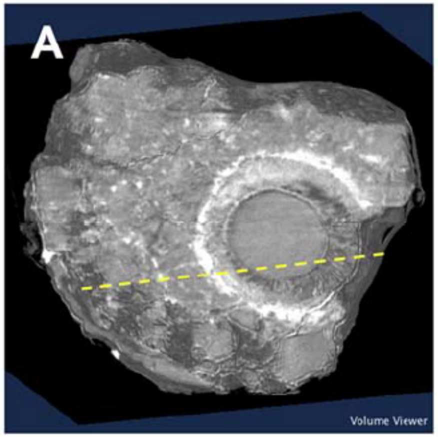
Melting of the upper mantle

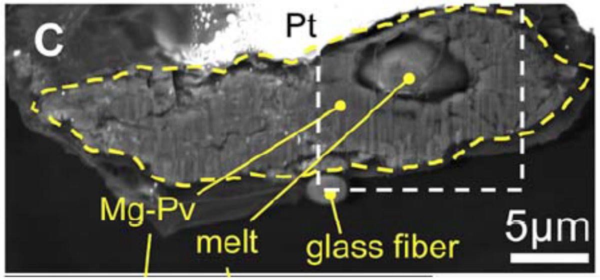


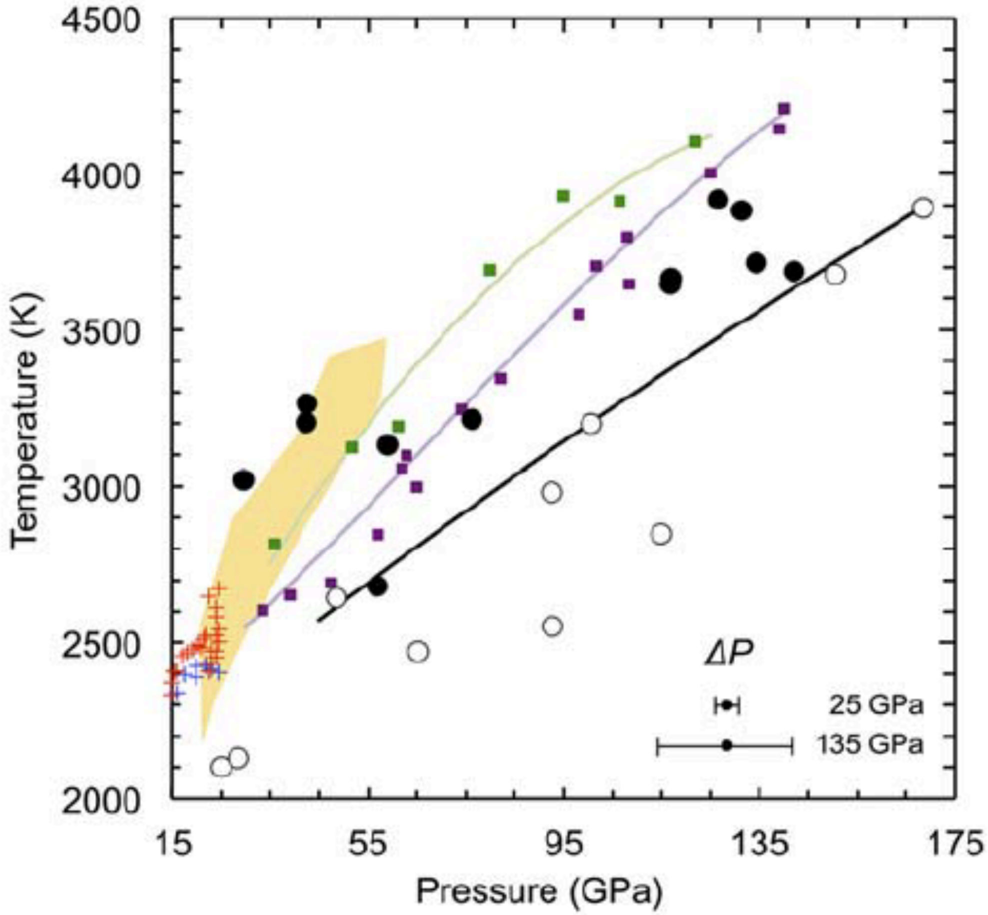


Sarafian et al., 2017

Melting of the lower mantle

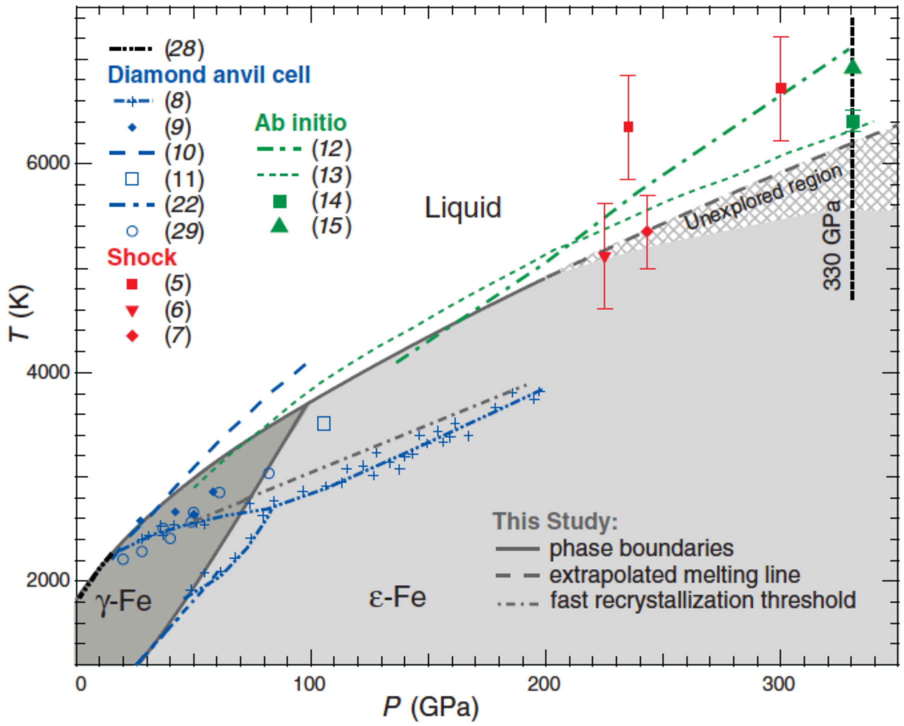




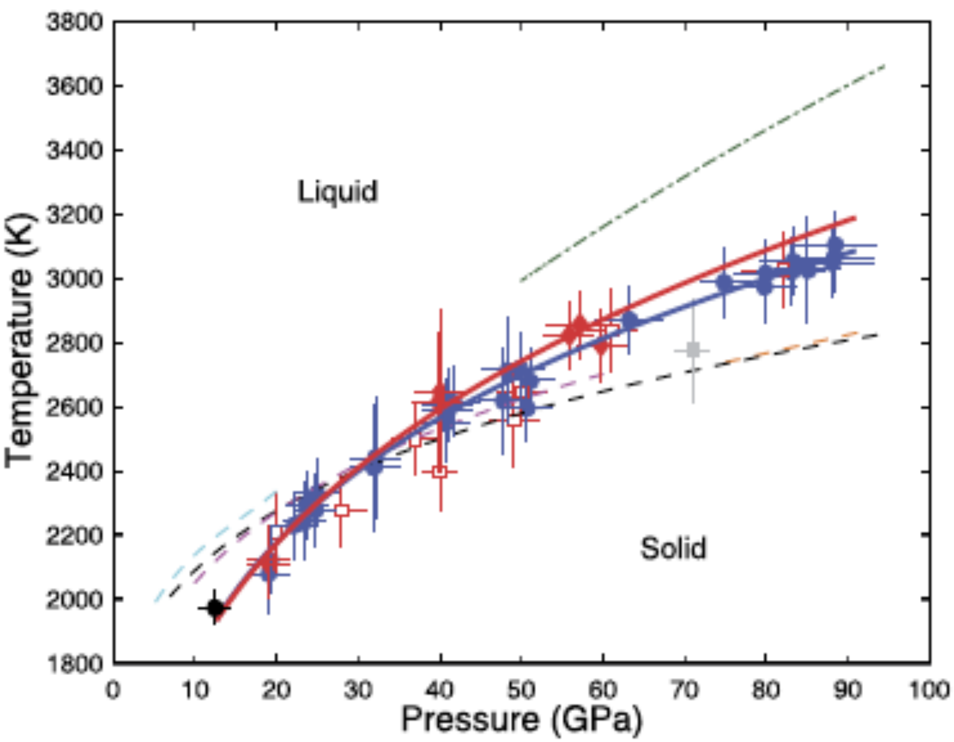


Nomura et al., 2014

Melting of Fe under core conditions



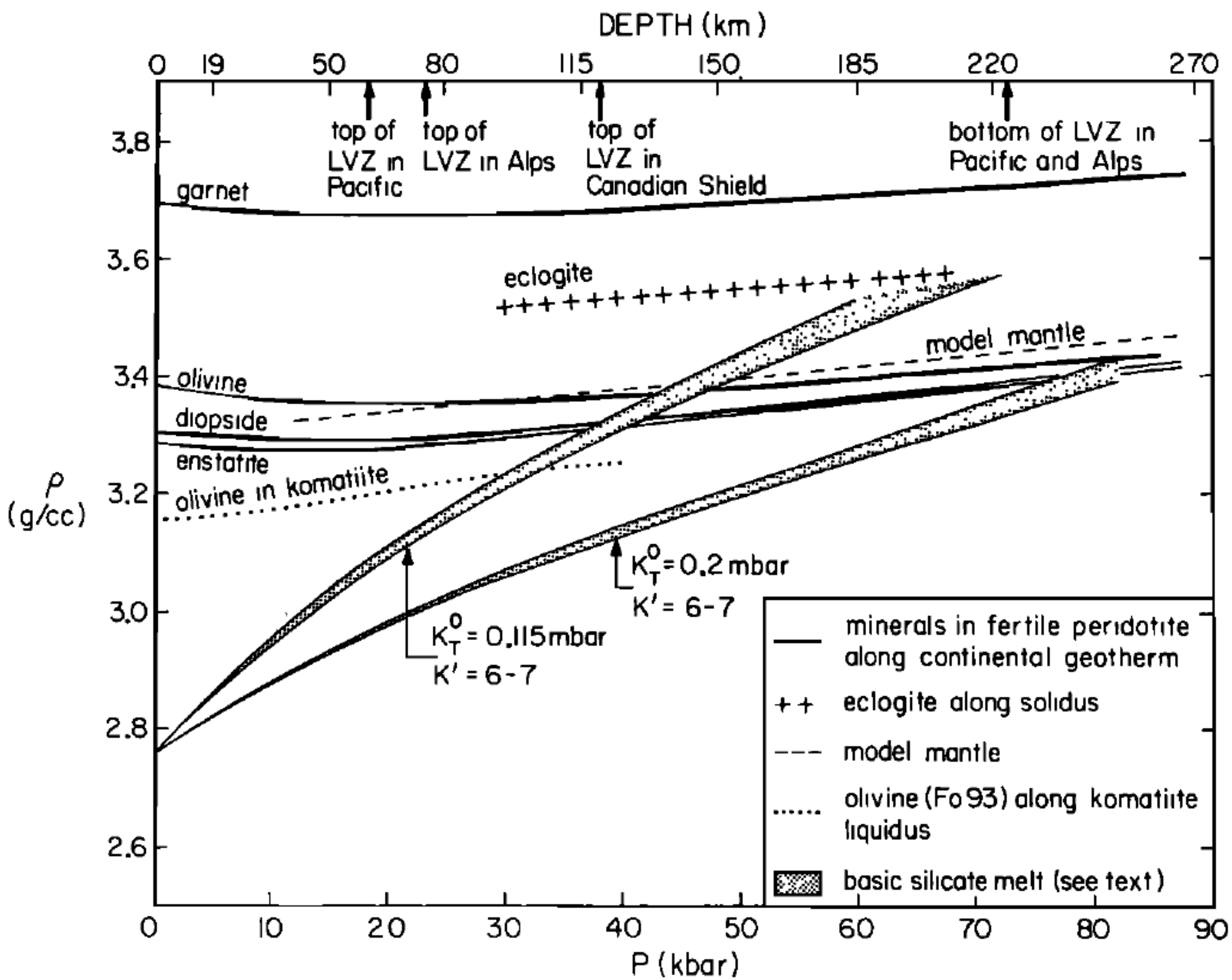
Anzellini et al., 2013



Zhang et al., 2016

2. Equations of state of melts

Stability of a melt layer in the mantle

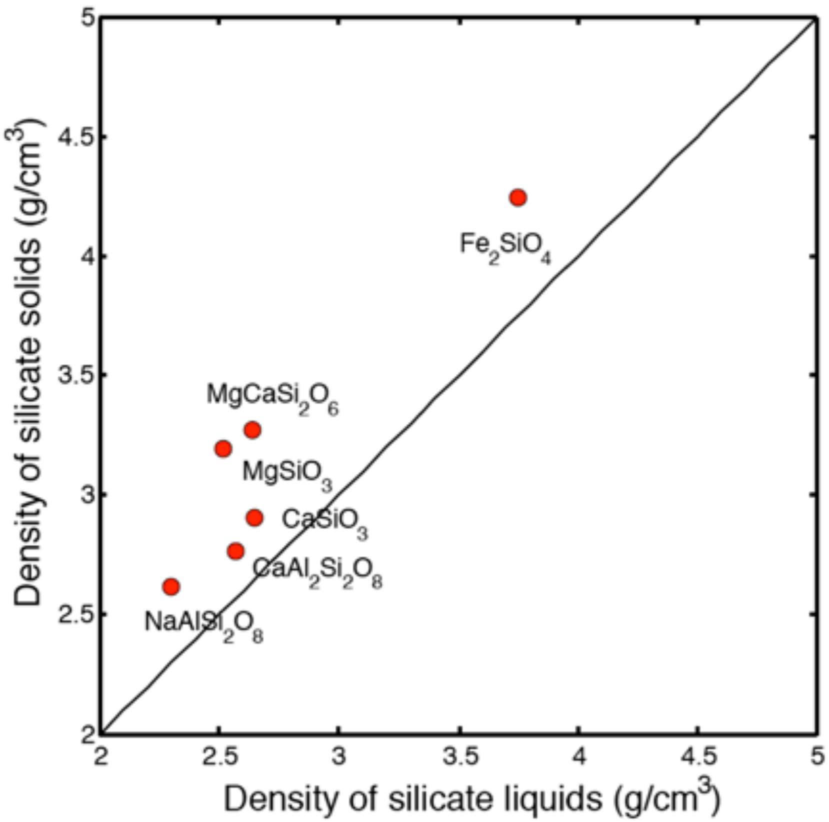


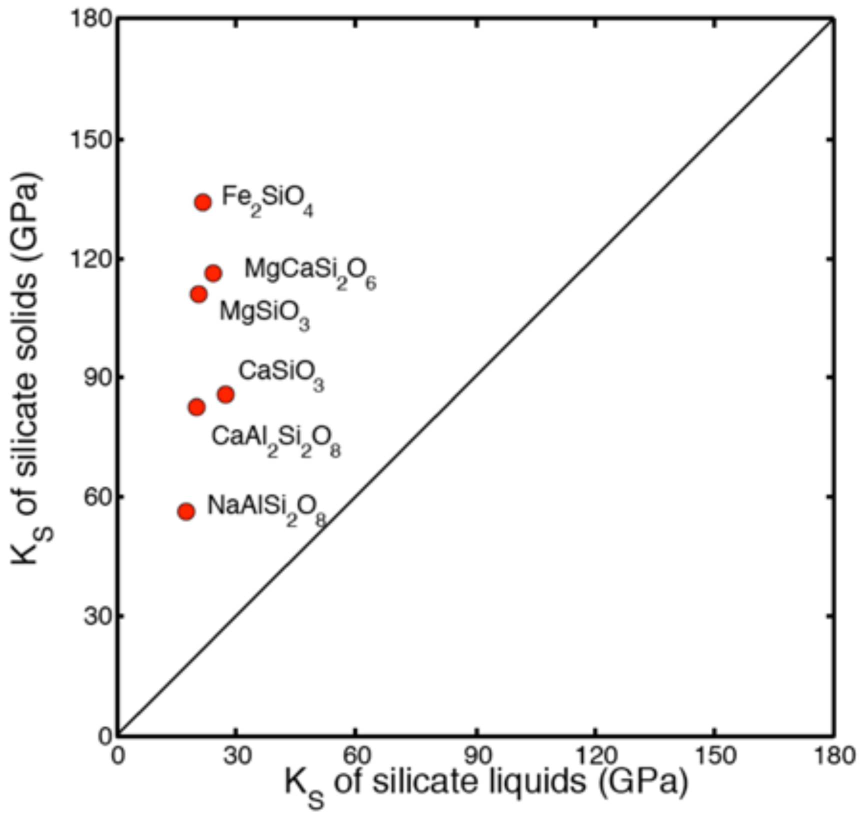
Stolper et al, 1981

Silicate melts vs silicate solids

$$\rho_0^{solid} > \rho_0^{liquid}$$

$$K_0^{solid} >> K_0^{liquid}$$





Silicate liquids are less dense but more compressible than solids at 1-bar.

Jing and Karato, 2011

Applying Birch-Murnaghan equation of state to melts

- Birch Murnaghan EOS

$$P = \frac{3}{2} K_{T0} \left[\left(\frac{\rho}{\rho_0}\right)^{\frac{7}{3}} - \left(\frac{\rho}{\rho_0}\right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4}(K'_{T0} - 4) \left[\left(\frac{\rho}{\rho_0}\right)^{\frac{2}{3}} - 1 \right] \right\}$$

- ρ_0 and K_{T0} are calculated by ideal mixing model (e.g., Lange, 1997; Ai and Lange, 2008; Ghiorso and Kress, 2004).

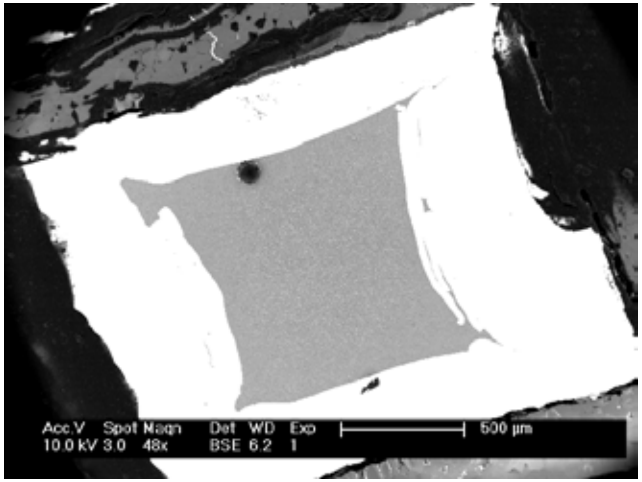
$$V = \sum_i X_i \left[\overline{V}_i + \frac{\partial \overline{V}_i}{\partial T} (T - T_{\mathrm{ref}}) \right]$$

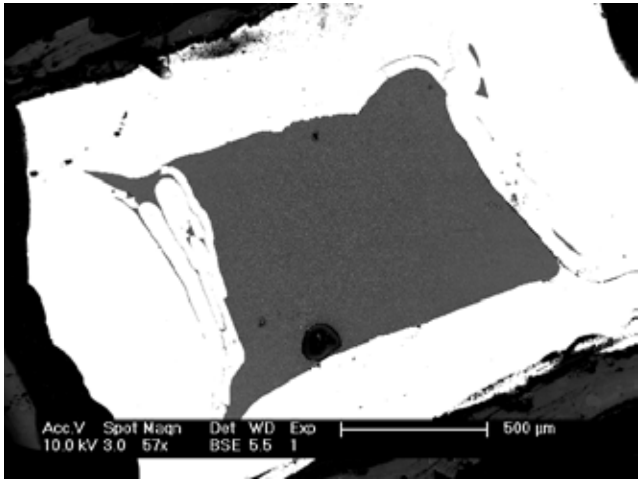
$$\frac{\partial V}{\partial P} = \sum_i X_i \left[\frac{\partial \overline{V}_i}{\partial P} + \frac{\partial^2 \overline{V}_i}{\partial T \partial P} (T - T_{\mathrm{ref}}) \right]$$

$$\rho_0(T, X) = \frac{V}{\sum_i X_i M_i} \qquad K_{T0} = -\left(V \frac{\partial P}{\partial V} \right)_0$$

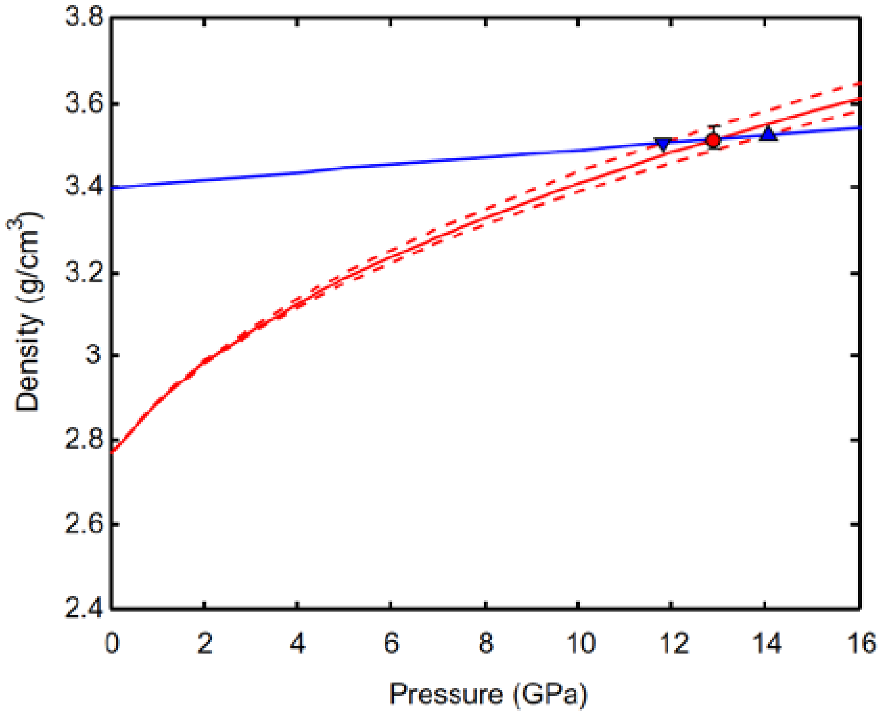
- K'_{T0} is constrained by high-pressure density measurements.

Sink/float method to determine density of melts at high pressures



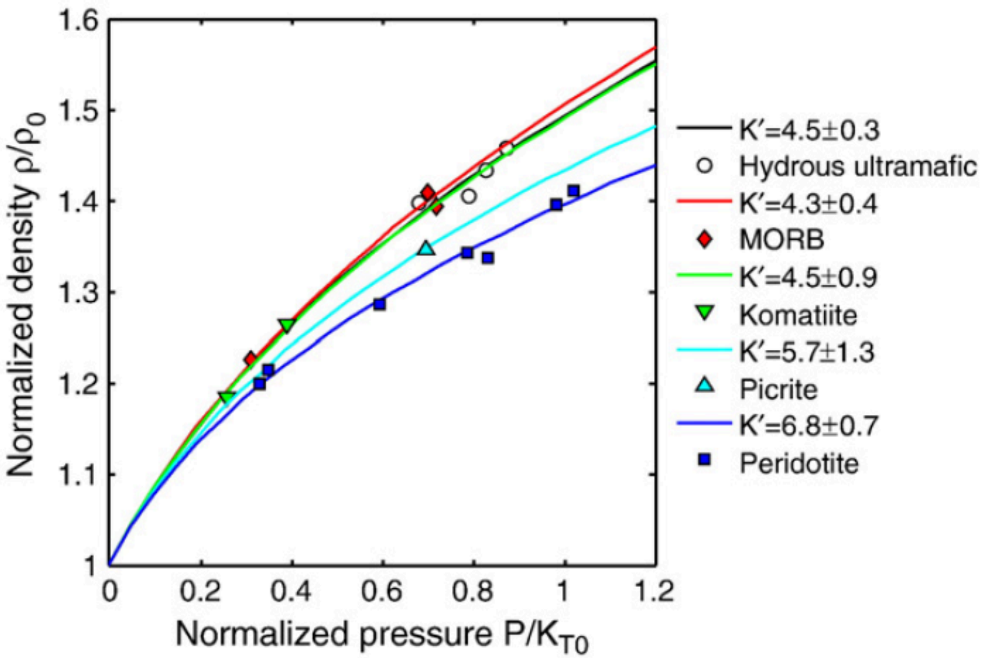


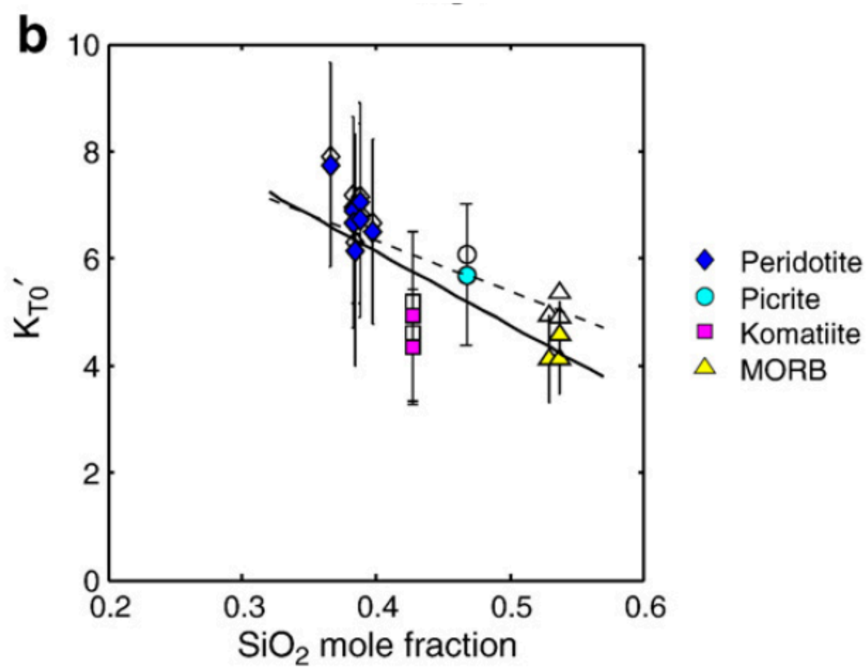
Up



Jing and Karato, 2012

Effect of composition on K'_T

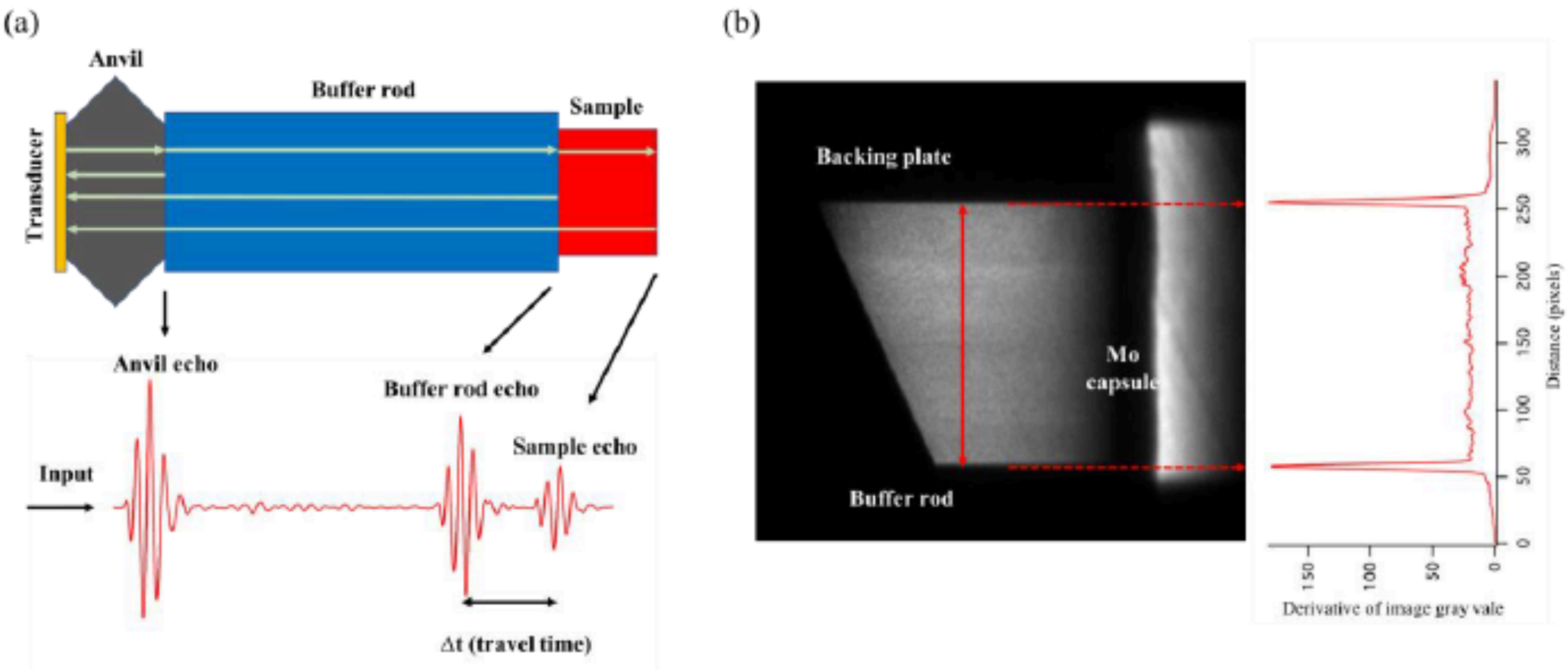




Jing and Karato, 2008

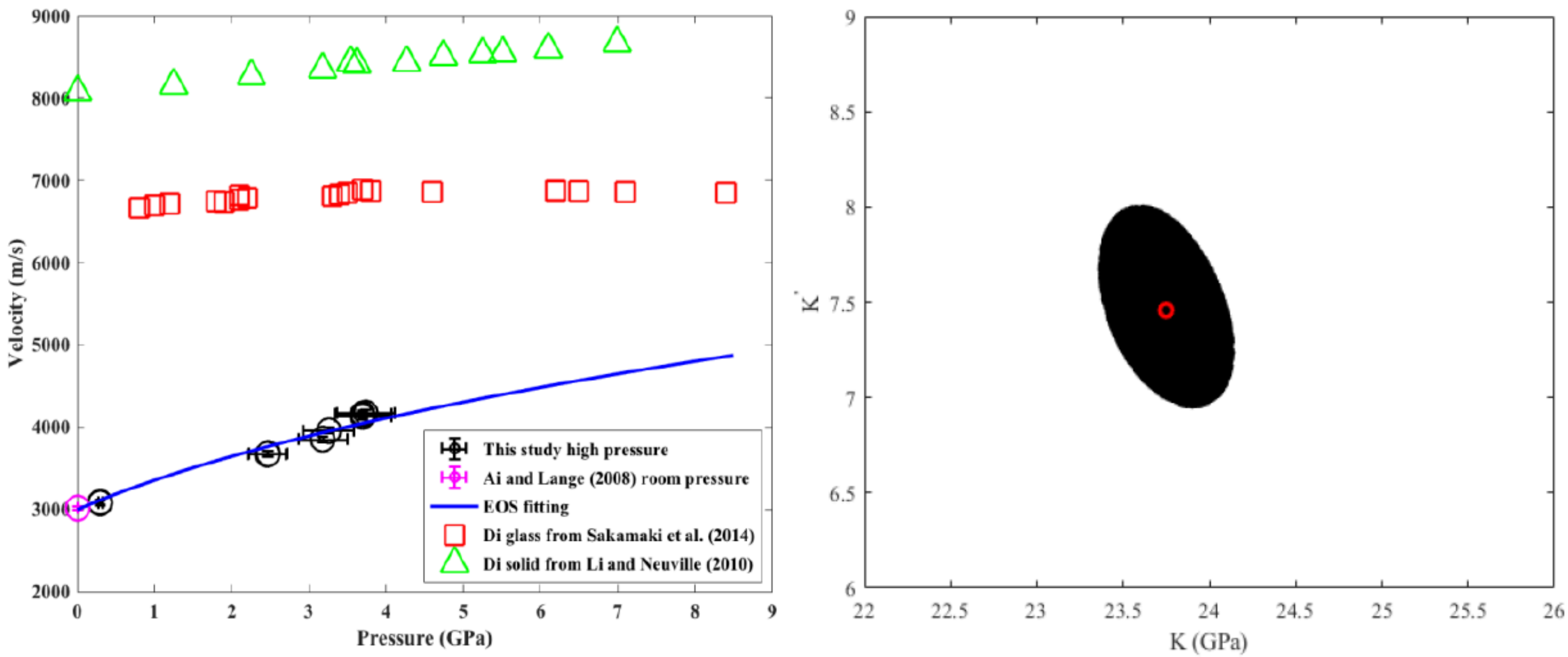
K’ has a large uncertainty due to the trade-off between K and K’

Ultrasonic sound velocity measurements to determine K and K’ at high P



Xu and Jing et al., submitted

Sound velocity of liquid diopside



Xu and Jing et al., submitted

Problems with the Birch-Murnaghan EOS

1. For each melt composition, at least one density or sound velocity data point at high pressure to is required to constrain K'.

2. Cannot be used to explain many distinct properties of melts because the EOS is not based on the physics of liquids.

Equation of state

- Helmholtz free energy of a system

$$F = U - TS$$

- Equation of state is given by taking volume derivative of *F*

$$P = P(V,T) = -\left(\frac{\partial F}{\partial V}\right)_T = -\underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{\text{Energy contribution}} + T\underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{\text{Entropy contribution}}$$

Mie-Grüneisen equation of state for solids

- Free energy has two parts

$$F = U_{T=0} + F_{th}$$

- For solids, F_{th} mainly comes from lattice vibration

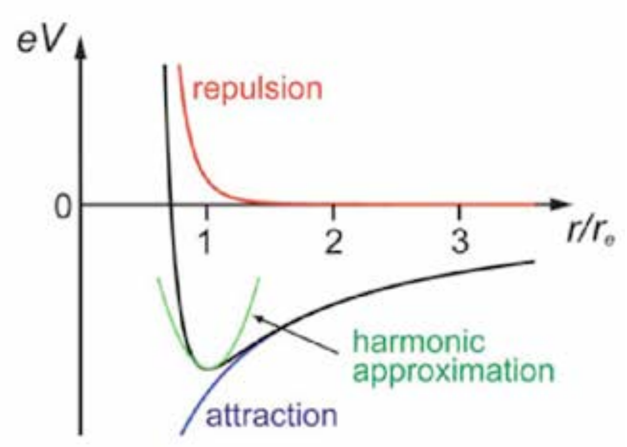
$$F_{th} = F_{vib} = U_{vib} - TS_{vib}$$

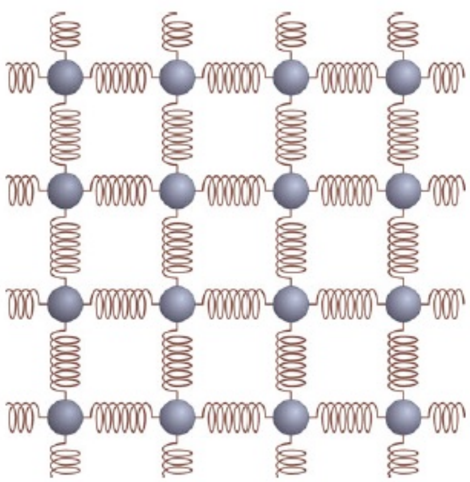
- Mie-Grüneisen EOS of solids

$$P = -\left(\frac{\partial U_{T=0}}{\partial V}\right)_T - \left(\frac{\partial F_{th}}{\partial V}\right)_T$$

$$P = \underset{\Rightarrow}{P_{T=0}} + P_{th} = P_{T=0} + \gamma \frac{U_{th}}{V}$$

Entropic contribution is small.





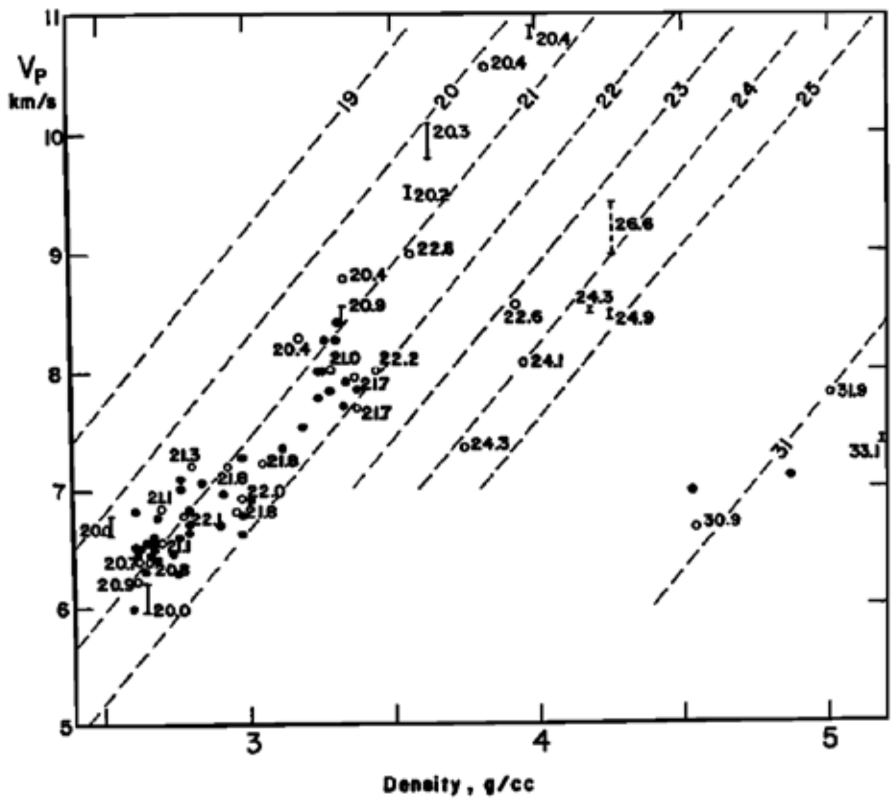
Böer and Pohl, 2014

Birch’s law of correspondence state

Birch’s law: Velocity of a solid material is a linear function of its density, regardless of the specific pressure and temperature conditions. That is,

$$V_p = a(\bar{M}) + b\rho$$

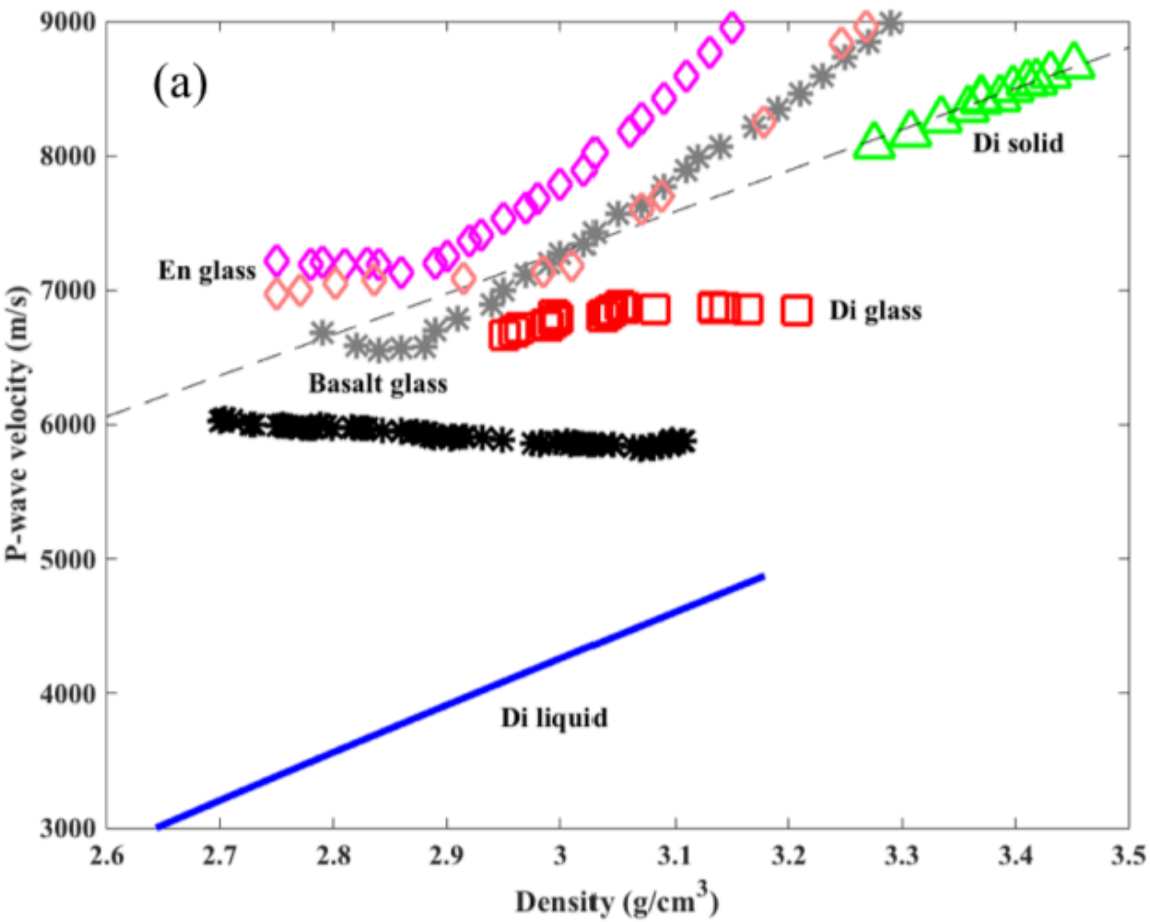
where a(M) is a constant depending on the mean atomic number



Birch, 1961

Silicate melts do not follow Birch's law

- Solids and glasses have the similar compression mechanism. But liquids have additional mechanisms.
- Entropic contribution is likely important for the compression of liquids.
- Liquids and glasses are fundamentally different in compressional properties. Glasses cannot be used as an analogy for liquids when studying compressional properties.



Xu, Jing, et al., submitted

Pressure dependence of Grüneisen parameter

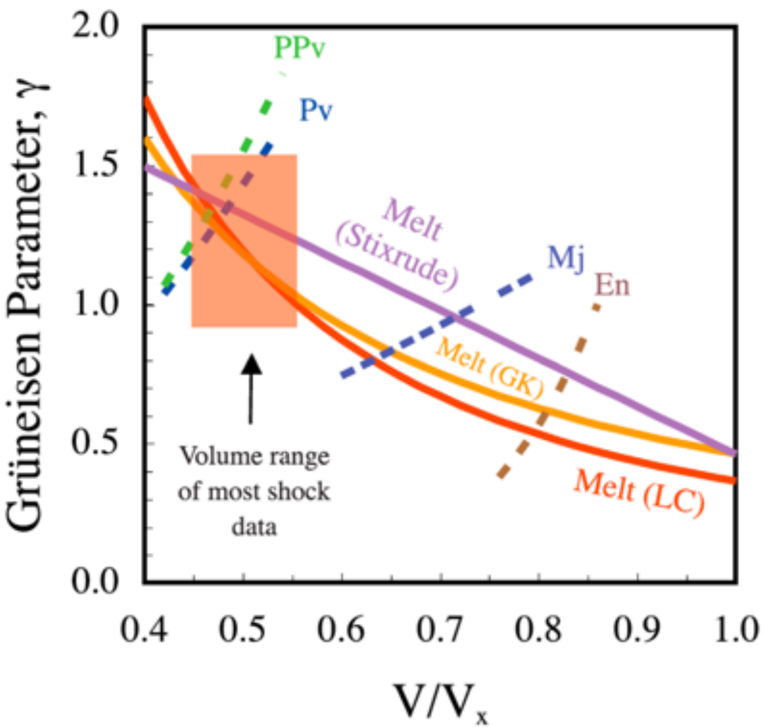
- Grüneisen parameter is defined as

$$\gamma = \frac{\alpha K_T V}{C_V} = \alpha_0 K_{T0} \frac{V}{C_V} \left(\frac{V_0}{V} \right)^{K_T' - \delta_T}$$

- For materials that follow Birch's law

$$\gamma \propto V \quad \text{or} \quad q = \frac{\partial \ln \gamma}{\partial \ln V} = 1$$

- But Grüneisen parameter increases with pressure for liquids (q<0).
- Liquids do not follow Birch's law.
- Entropic contribution to compression must be important.



Mosenfelder et al., JGR, 2009

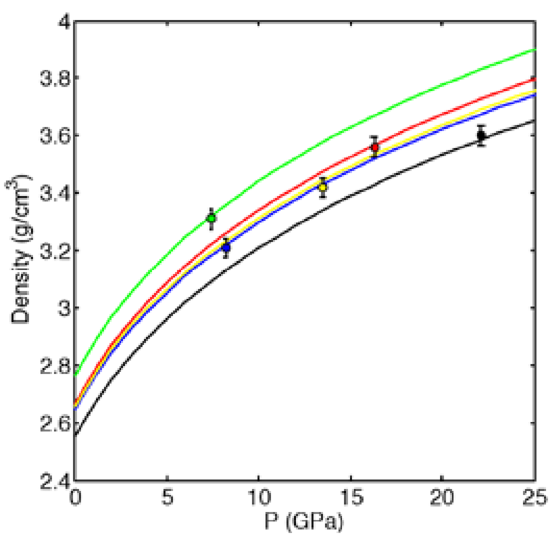
Equation of state based on hard sphere mixtures

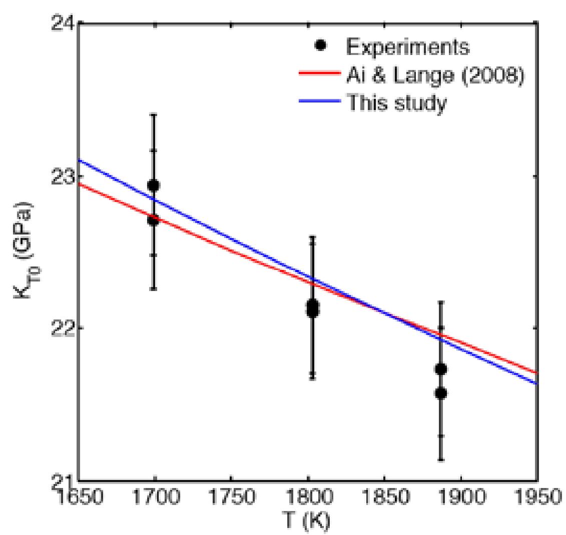
$$P = \frac{RT}{\overline{V}}\left[(1-\xi)\Phi - \Phi_0\left(\frac{\overline{V}_0}{\overline{V}}\right)^{\mu-1} + \xi\Phi_0\left(\frac{\overline{V}_{m0}}{\overline{V}_m}\right)^{\nu-1}\right]$$

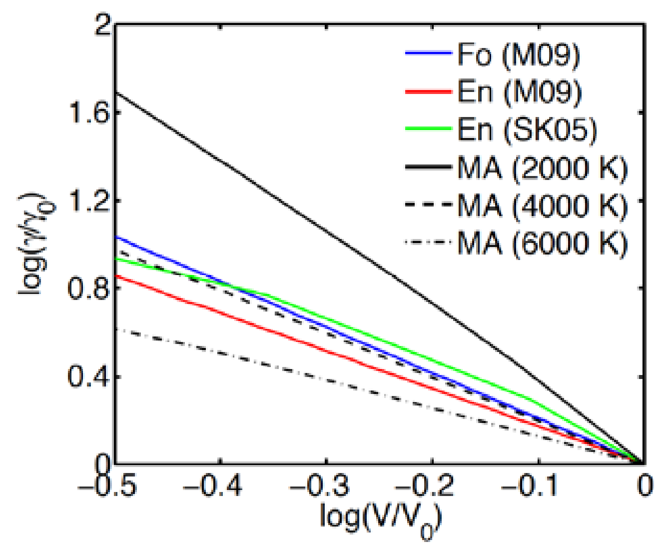
Kinetic energy (entropy)

Attractive force

Repulsive force



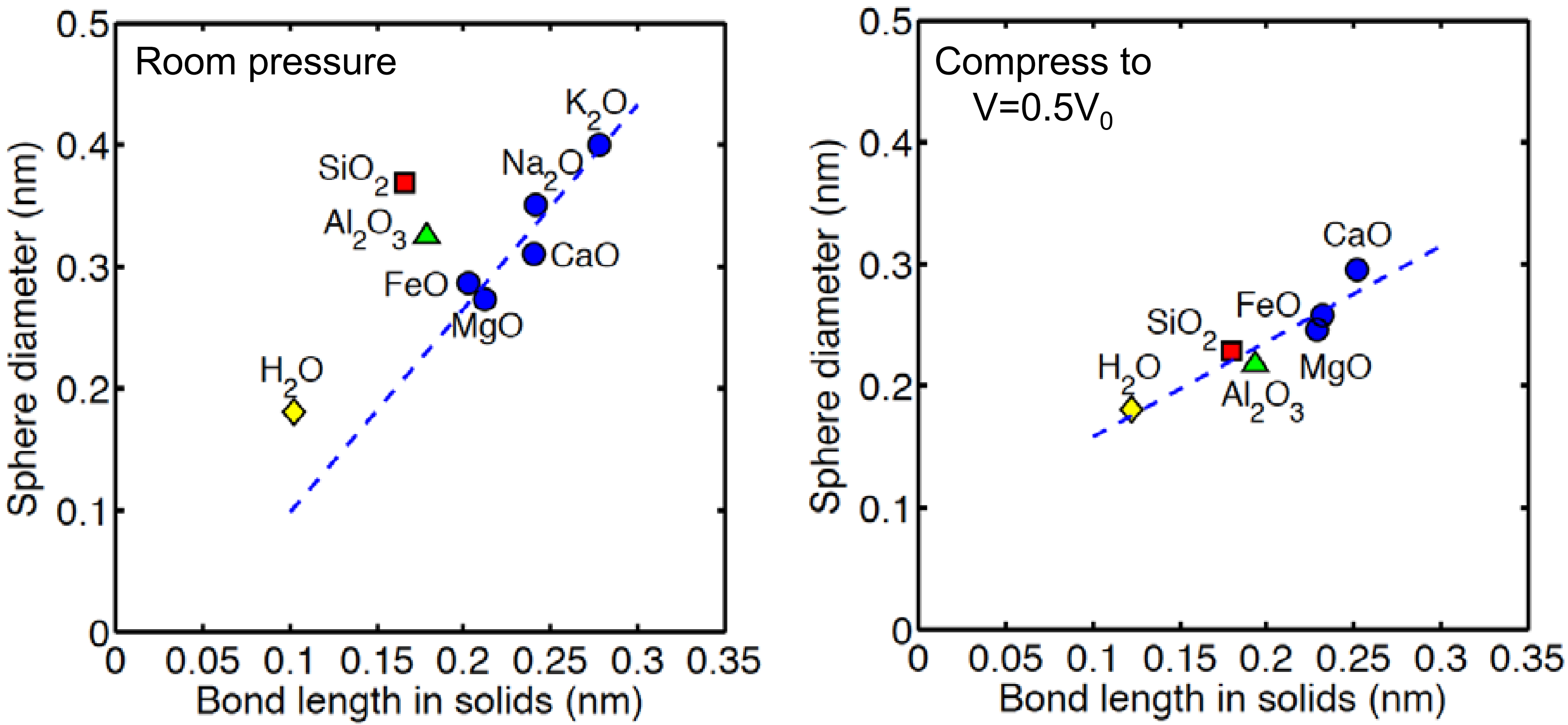




Jing and Karato, 2011

Comparison of sphere diameters with bond lengths in solids

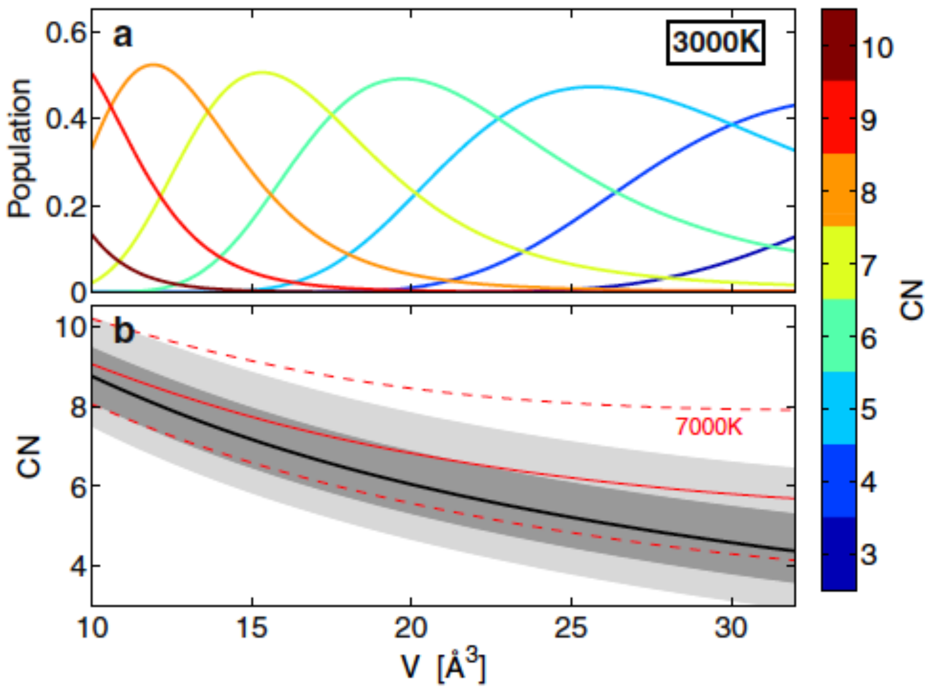
- The correlation between sphere diameters and bond lengths suggests that the short-range order of liquids is correctly represented in the hard sphere model.

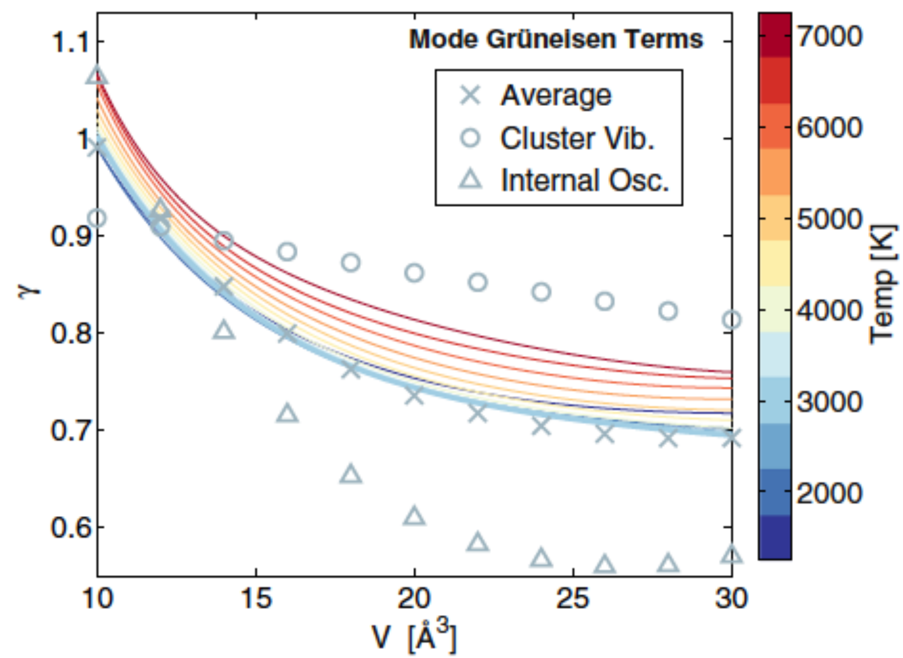


Jing and Karato, 2011

Coordinated hard sphere mixture model

- Coordination of cations is explicitly modeled.
- Currently only available to MgO melt

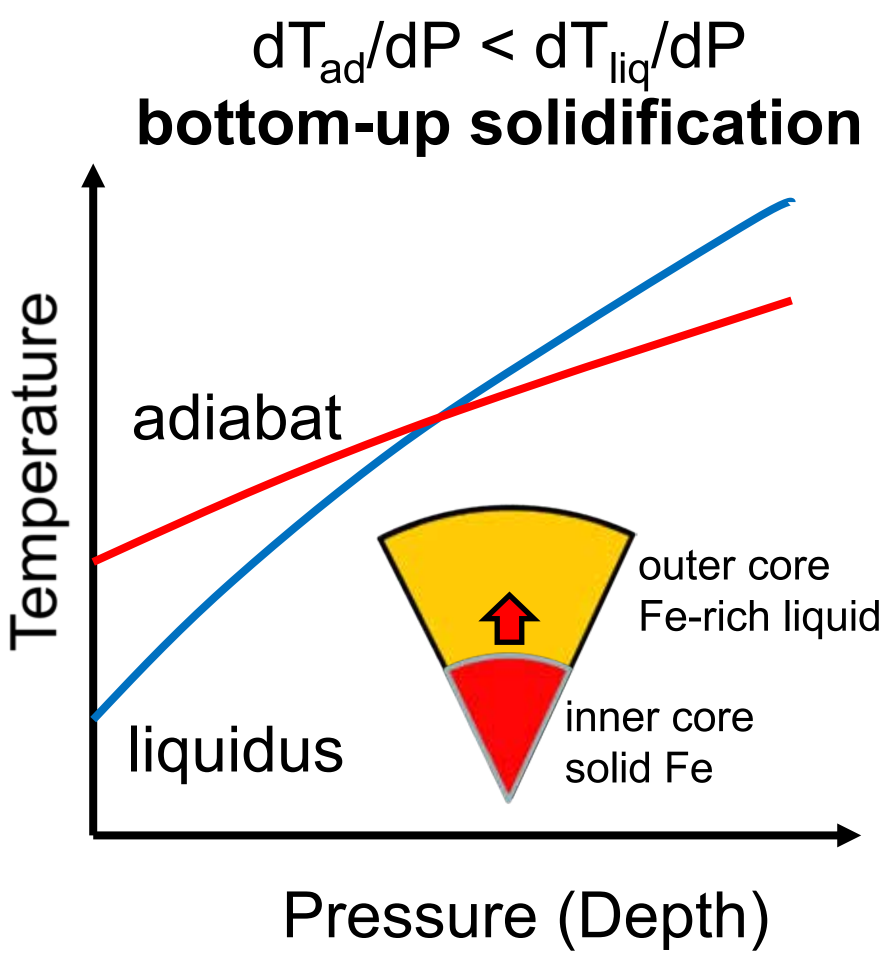


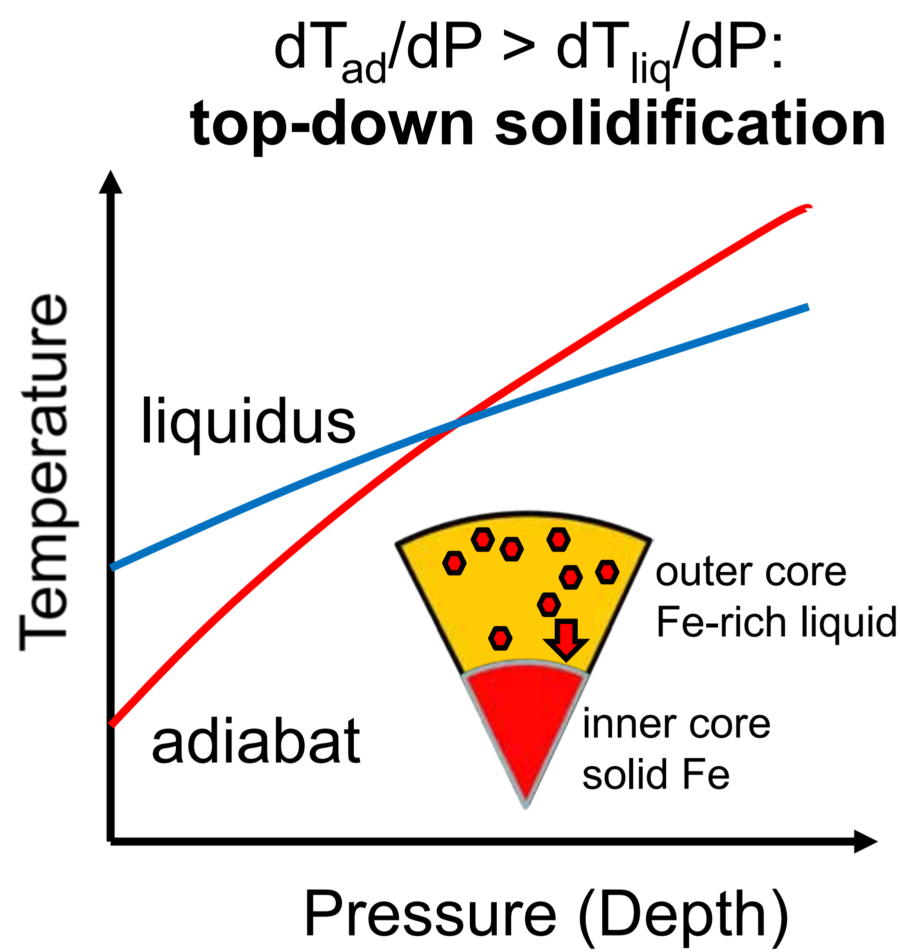


Wolf et al., 2015

3. Solidification of melts

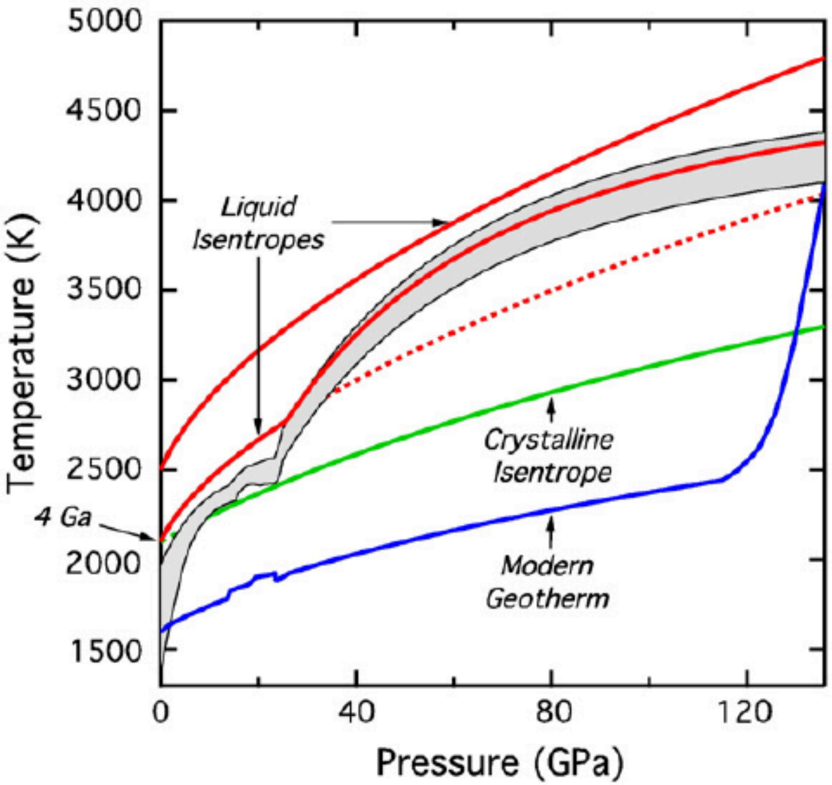
Solidification of a melt layer in planetary interiors



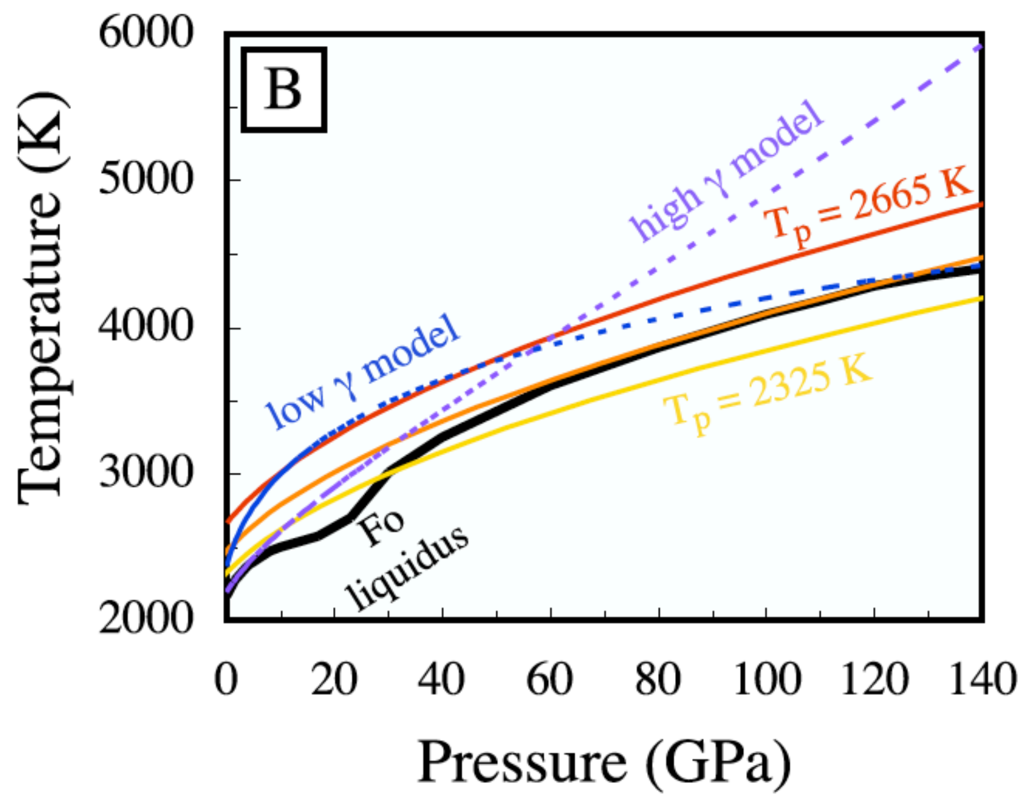


The adiabatic temperature gradient is related to the **temperature dependence of sound velocity** of the liquid

Solidification of a silicate magma ocean

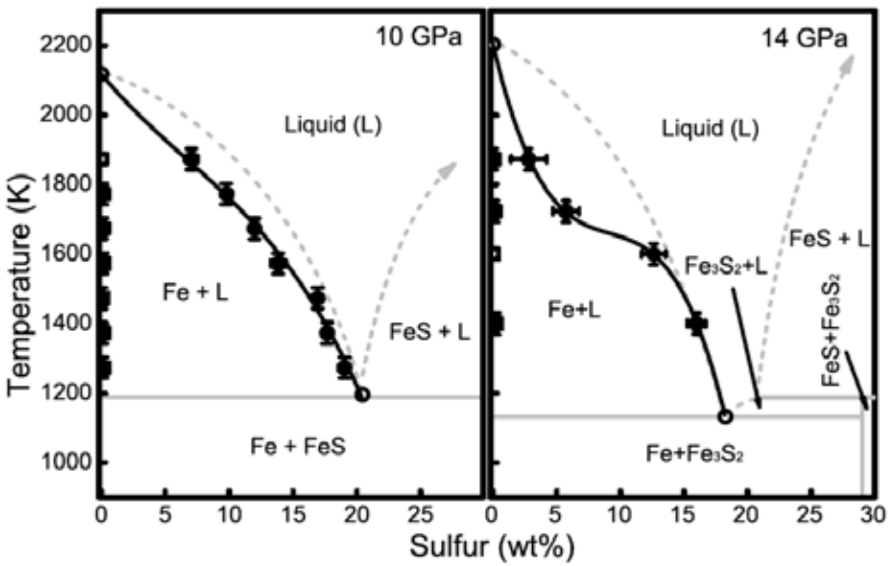


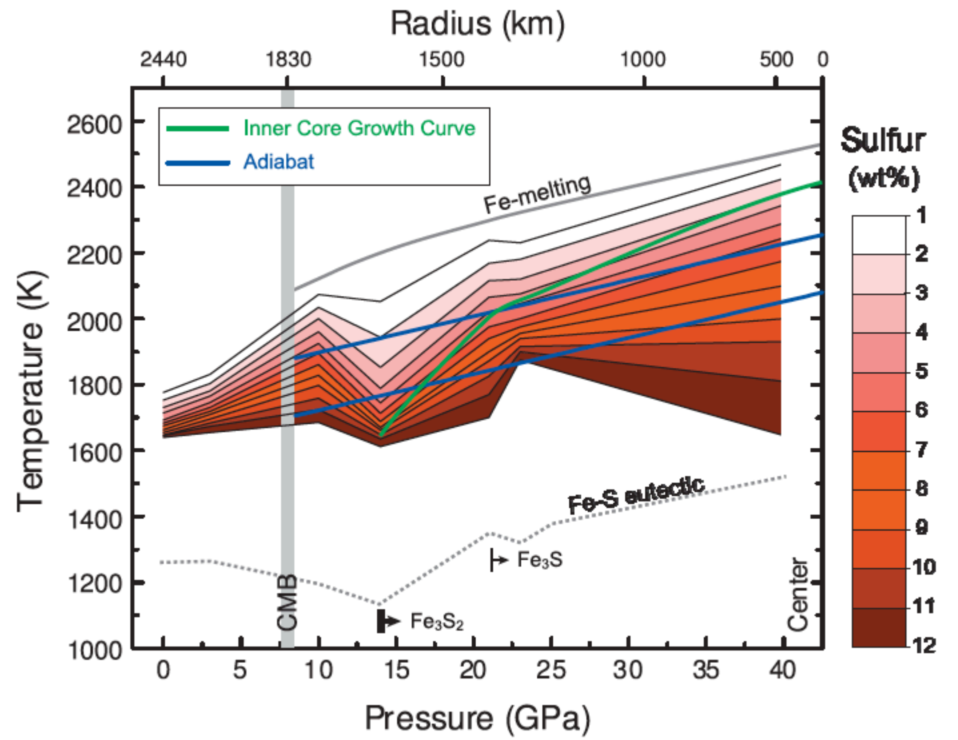
Stixrude et al., 2009



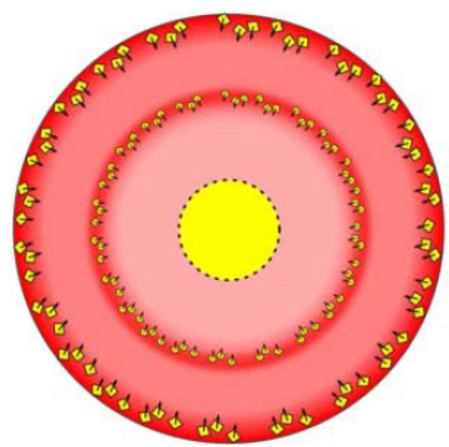
Mosenfelder et al., 2009

Double snowing core in Mercury



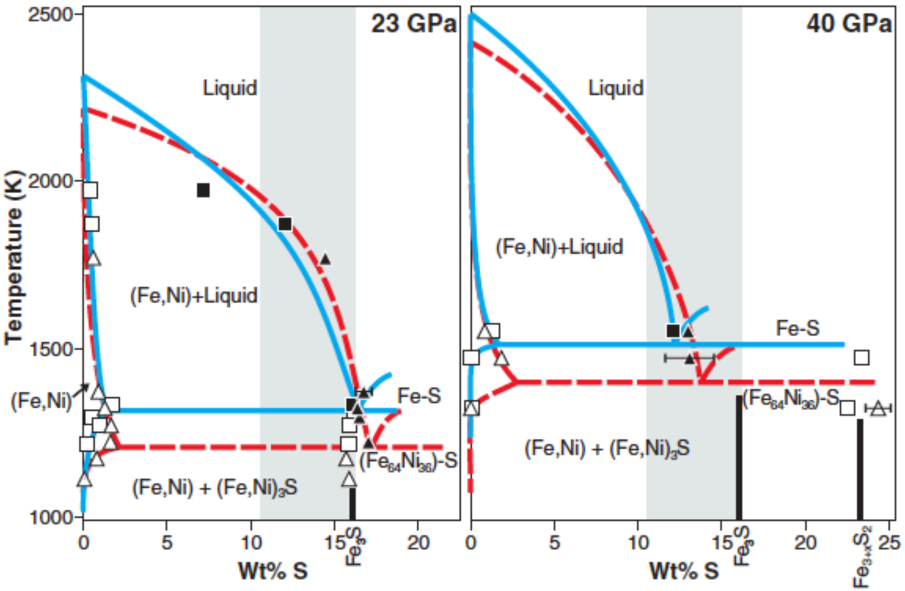


Chen et al., 2008

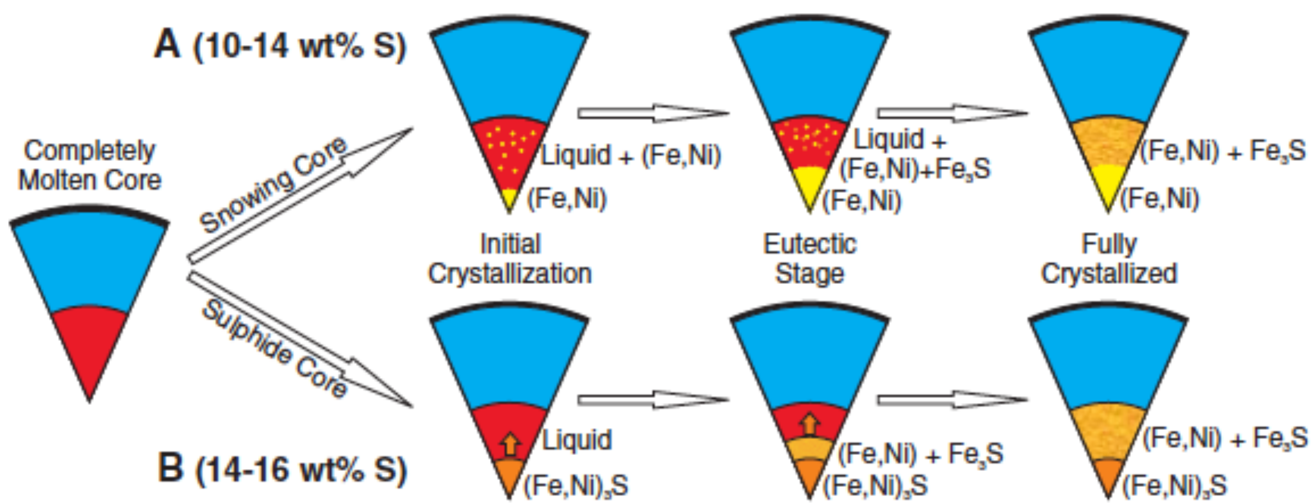


Double-snow state

Solidification of the Martian core



Stewart et al., 2008



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Earth's inner core nucleation paradox

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