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Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

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Departement Erdwissenschaften

Doctoral School – Les Houches

Geochemistry

Compositional Heterogeneity in the Mantle through Time

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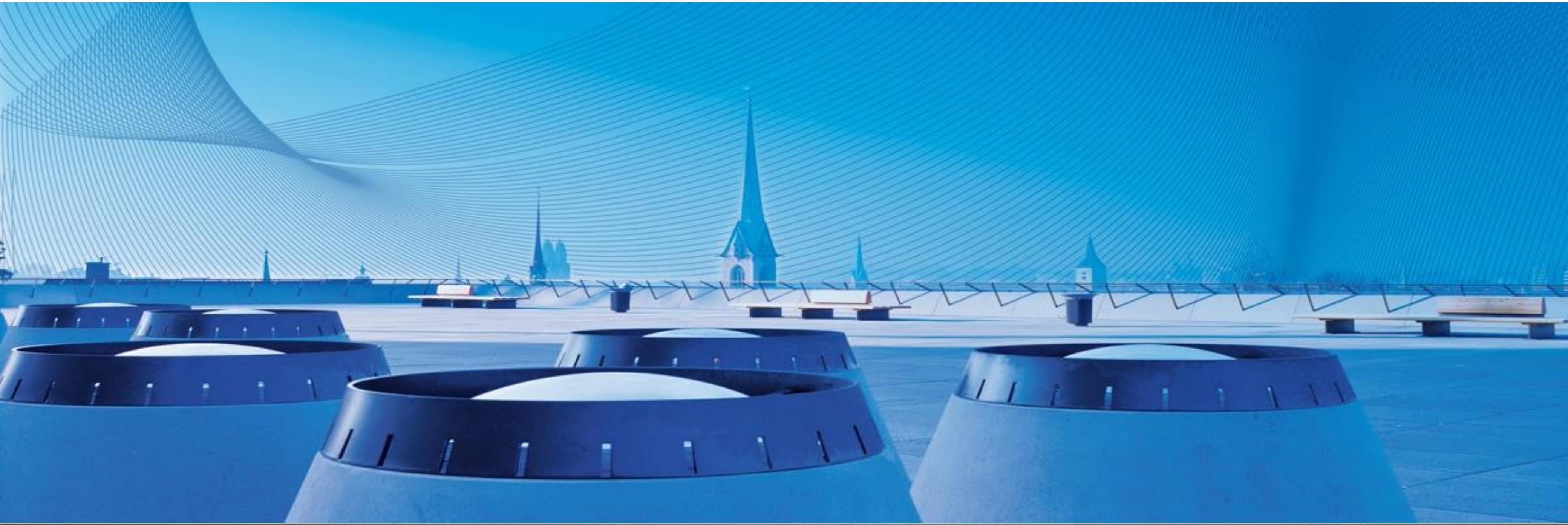


Overview

- **Mantle composition and its importance**
  - History
  - Assumptions and models
- **The message from peridotites**
  - Compositional variability among peridotites
  - Diversity of mantle lithologies
  - Partial melting of heterogeneous mantle
- **Mantle geochemical evolution as told by komatiites**
  - Archean mantle temperatures
  - Trace element compositions
  - Secular chemical trends

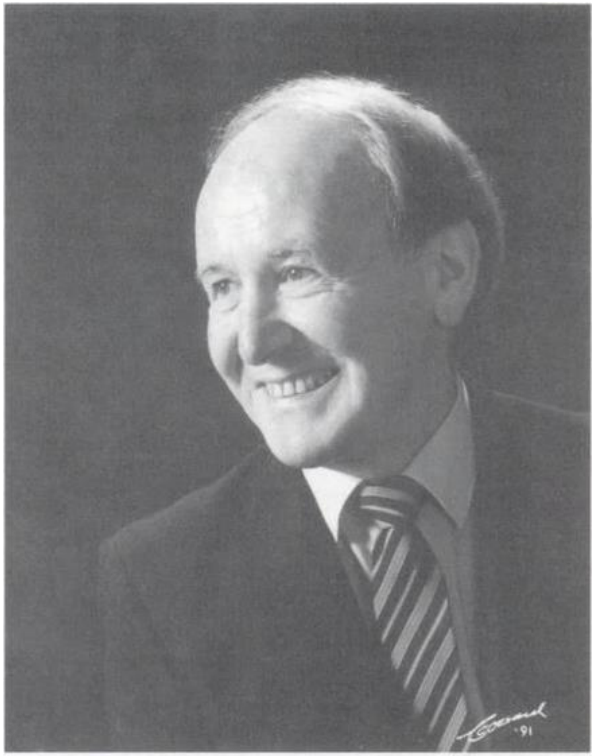
What is the composition of the Earth's mantle?

1. Cosmochemical constraints
2. Indirectly, through:
   - mantle melts
   - geophysics (density, seismic waves, heat flux)
3. Directly, through study of mantle samples

Pyrolite

- Pyrolite = Pyroxene – Olivine – ite
- Ringwood 1962
- The ‘cosmochemical’ model
- Considered the Earth as conforming to the chondritic model

Lead to the concept that ultramafic rocks on Earth came from its mantle



A. E. (“Ted”) Ringwood (1930–93)

Primitive Mantle – Cosmochemical Constraints

Using solar (CI) abundances, assuming all refractory lithophile elements are present in chondritic proportions, and the mass of the core (assumed 85% Fe) relative to the mass of the BSE (0.32:0.68):

Oxide component	Concentration (wt%)
MgO	35.3 (*36.8*)
SiO_2	50.9 (*45.4*)
FeO	7.3 (*8.1*)
Al_2O_3	3.6 (*4.5*)
CaO	2.9 (*3.7*)

Actual composition in brackets

With adjustment of FeO to reflect oxidation state, hence core size, this composition can be regarded as the default composition for the silicate portion of any terrestrial planet or differentiated rocky object

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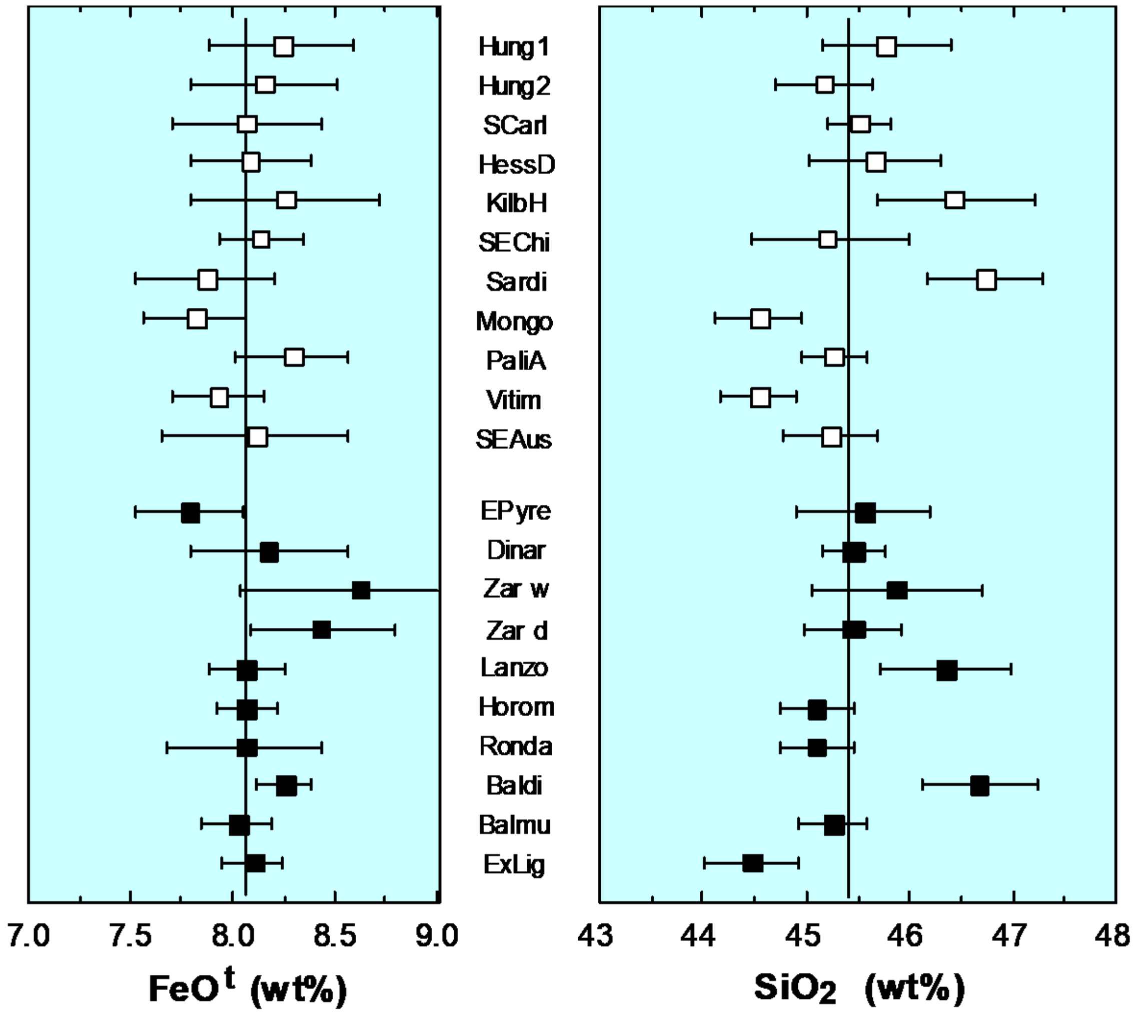
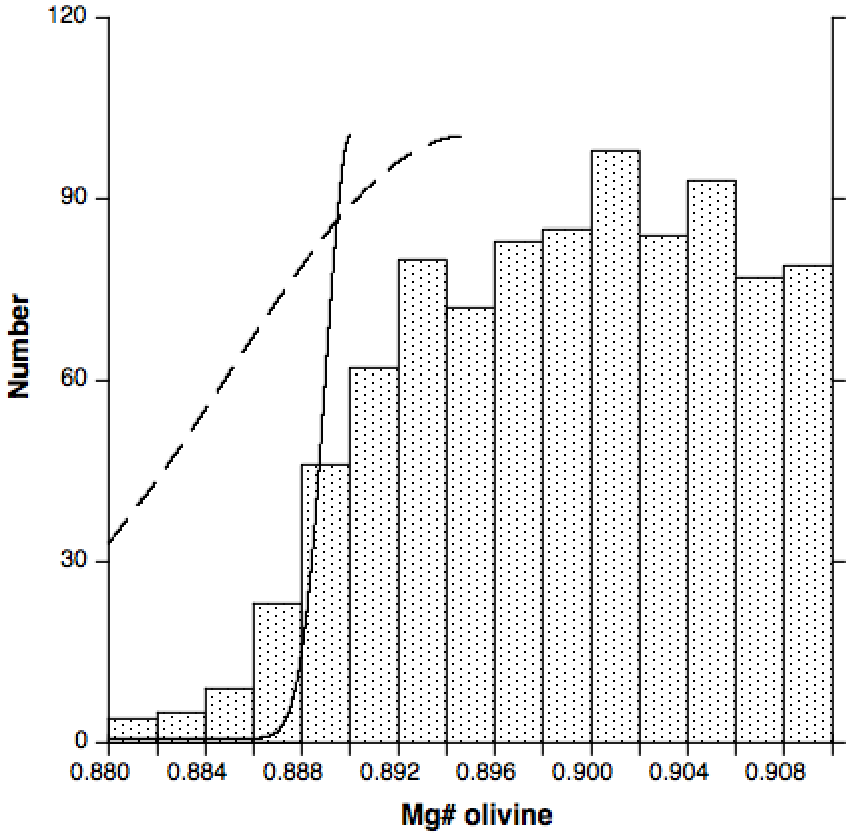
Primitive Mantle Algorithm



Primitive Mantle Algorithm

Histogram of Mg#s in mantle spinel peridotites



Primitive Mantle Algorithm

(6 unknowns, 6 constraints)

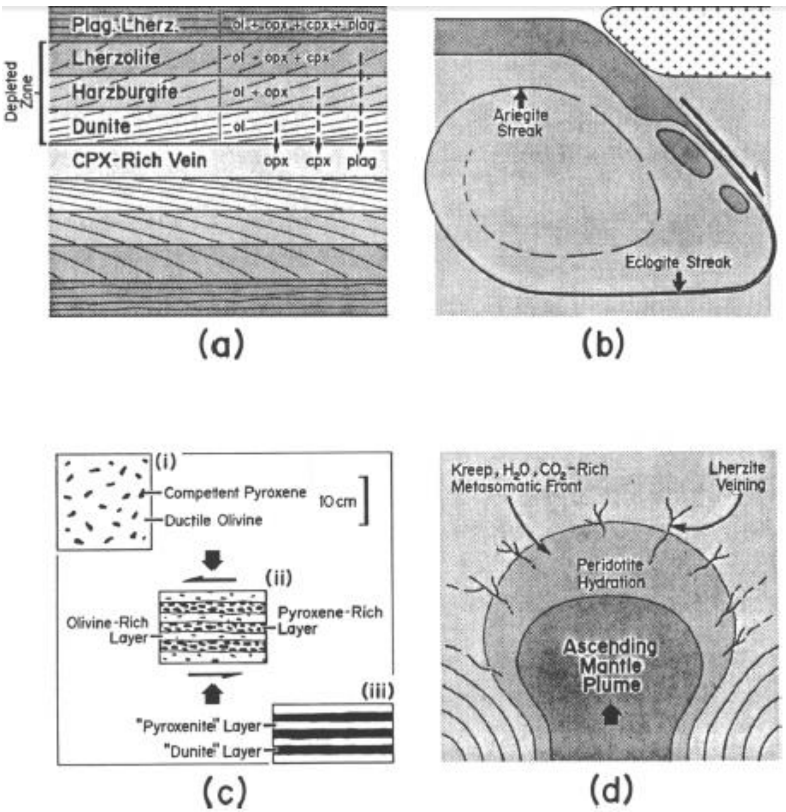
1. O is fixed by stoichiometry ($Fe^{3+}/\sum Fe = 3\%$)
2. FeO^t is constant at 8.10 ± 0.05 wt%
3. Molar Mg/(Mg+Fe) of least depleted samples is 0.890 ± 0.001

   Therefore BSE MgO is 36.8 ± 0.4 wt%
4. SiO_2 is nearly constant - intercept at 36.8 wt% MgO is 45.4 wt%
5. $CaO + Al_2O_3 + SiO_2 + FeO = 98.54^* - MgO - FeO_t - SiO_2$ wt%
6. Ca and Al are Refractory Lithophile Elements, chondritic CaO/Al_2O_3 is 0.79

* Na_2O, TiO_2, Cr_2O_3, MnO and NiO make up 1.36 wt% of the remaining 1.46 wt%

The real mantle

Processes complicating interpretation of samples of the real mantle are:



Spray, 1989

Partial Melting (a)

- Extraction of the continental crust → depleted mantle (source of MORB & oceanic crust)

Physical (b)

- Mechanical mixing of fertile with depleted mantle by stirring during mantle convection

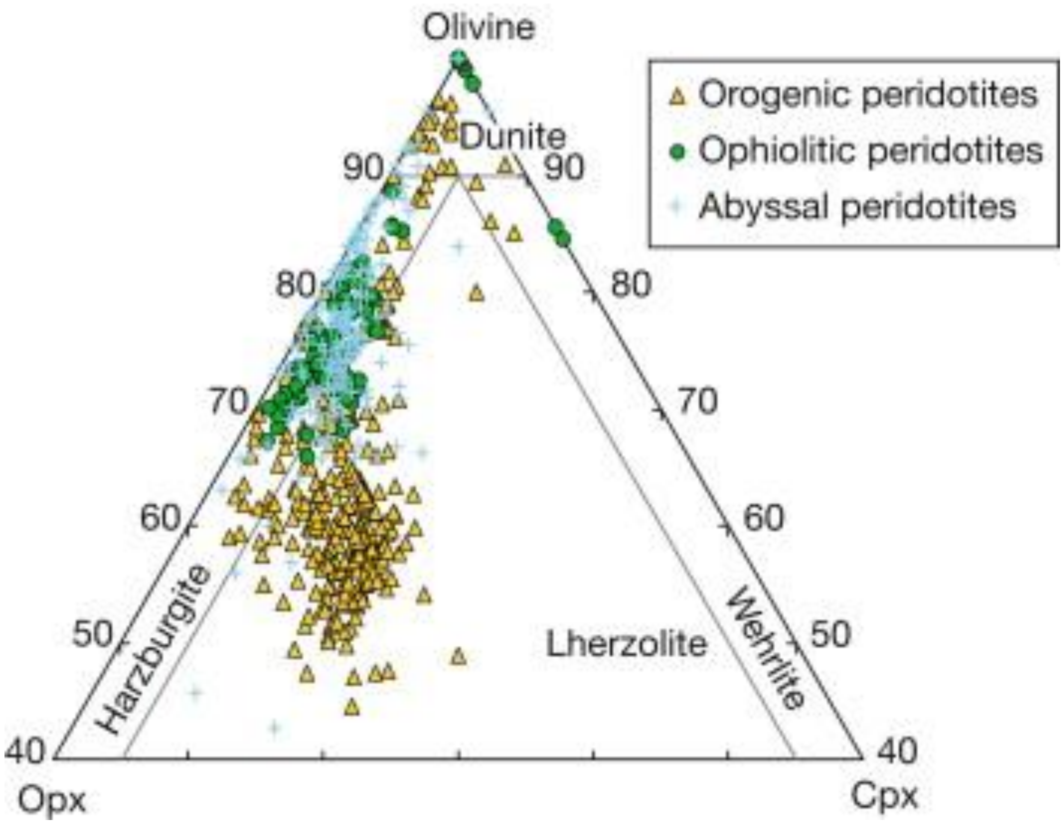
Metamorphic (c)

- Cooling and subsolidus re-equilibration after melt extraction
- Modal inhomogeneity - metamorphic differentiation

Metasomatic (d)

Metasomatism in the lithosphere (e.g., contamination by later melts or fluids)

Peridotite types



Bodiner and Godard (2003)

Orogenic

- Typically lherzolitic in composition, unrelated to ophiolitic ocean crust (Menzies and Dupuy, 1991)
- Typically ~1 - 10 kms in size

Ophiolitic

- Near-complete sections through oceanic crust/suprasubduction zones (Nicolas, 1989)
- > 10s kms in size

Abyssal

- Often rich in olivine/opx
- Hydrothermally altered

Orogenic peridotites

Orogenic peridotite massifs, large volumes of mantle exposed on the Earth's surface, comprise:

1. 70% Lherzolite
2. 20-25% Harzburgite + Dunite
3. 5-10% Mafic lithologies

Are *metamorphic rocks* layered on the cm- to m-scale

Balmuccia, Italy

A primitive mantle 'concept' is purely hypothetical, the picture in the mantle is much more complex

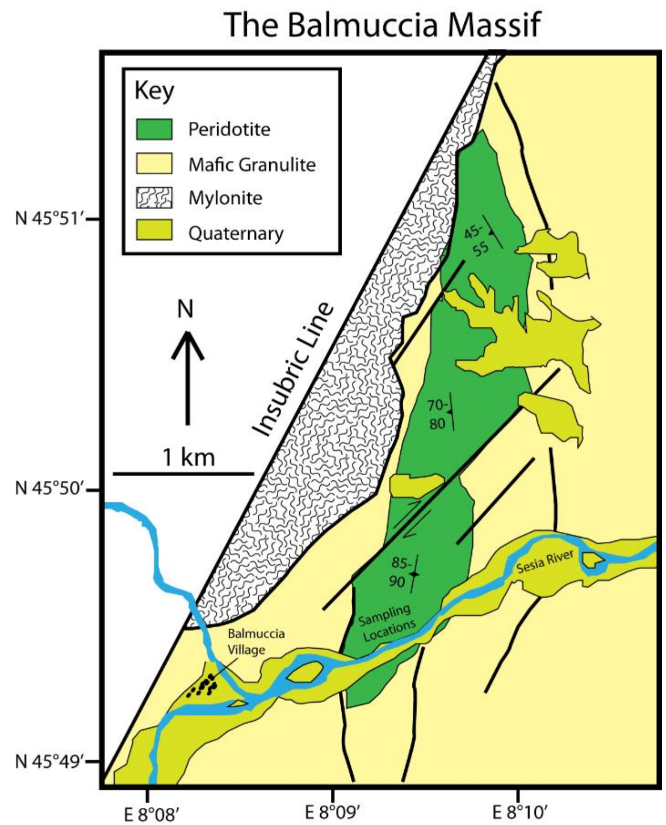
Balmuccia Lherzolite

The Balmuccia massif is a km-scale lherzolite body

Does **not** define a petrologic moho (Quick et al., 1995)

The peridotite has favourable traits for studying processes occurring in the mantle:

1. Fertile
2. Fresh
3. Unmetasomatised
4. It’s Italian

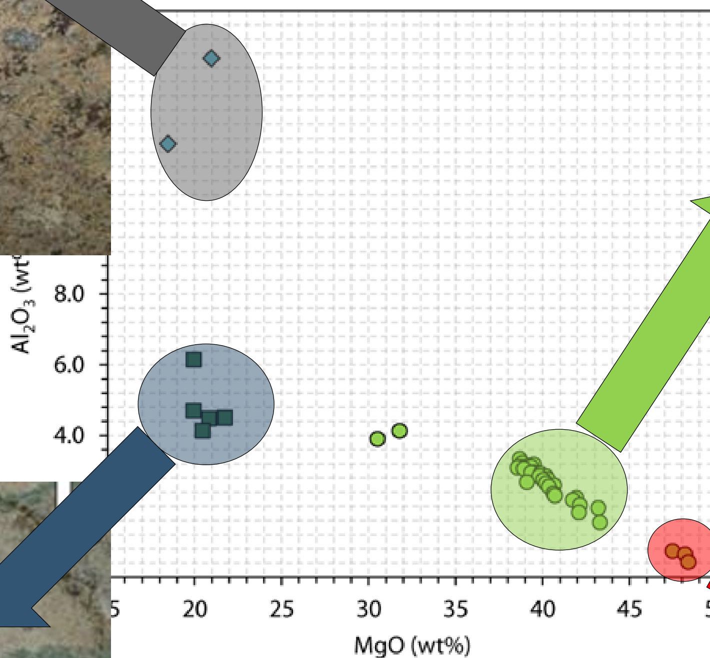


Balmuccia Massif

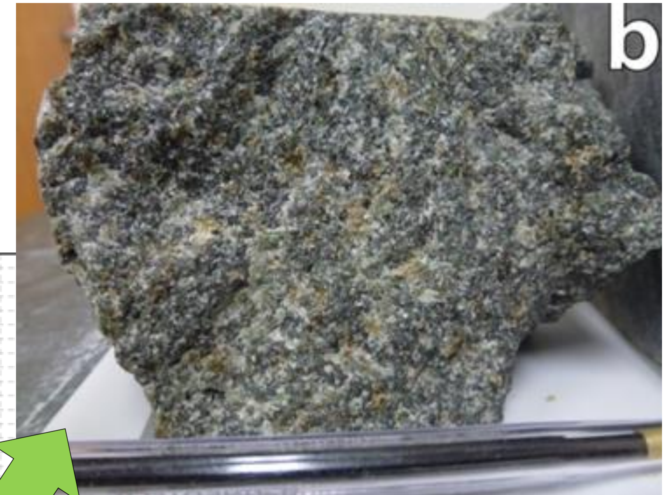
Pyroxenites

Al-Augite

Chrome-Diopside



Peridotites

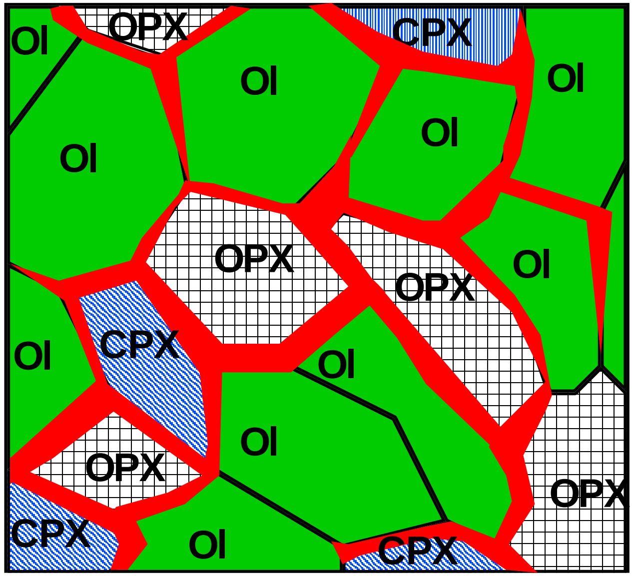


Lherzolite

Dunite

Partial melting

Phase change **solid** → **liquid** in response to changing P, T, X



Peridotite
~55 % olivine
~25 % orthopyroxene
~18 % clinopyroxene
~2 % spinel

Batch melting

- Melt in equilibrium with solid
- Irrespective of P-T path, initial melt fraction

Fractional melting

- Infinitesimal amount of melt extracted
- Composition of residue changes

Partial melting

Experiments of phase relations of fertile peridotite (O'Hara, 1968; Jaques & Green, 1980; Kinzler and Grove 1992; Walter, 1998)

It is the **minerals** that melt, **not** the bulk composition

Reactions written in the form:

x orthopyroxene + *y* clinopyroxene = *z* olivine + (1-*z*) melt

Results in systematic changes to composition of the residue

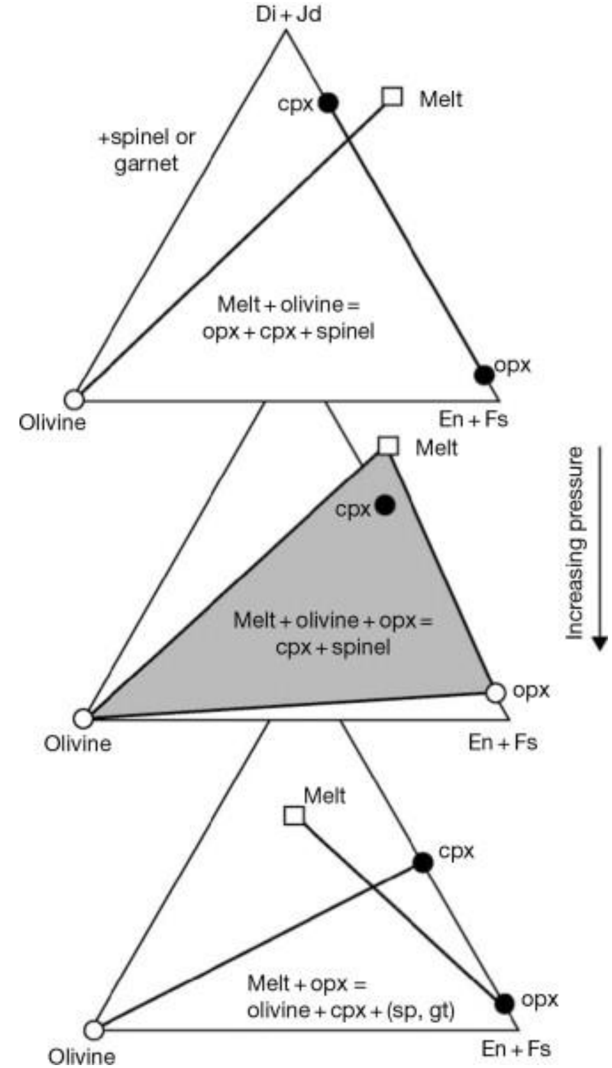
Partial melting

Compositions and stabilities of minerals change with *P, T*

Low Pressure
cpx, opx unstable; ol produced
35 opx + 60 cpx + 5 sp = 80 liq + 20 ol

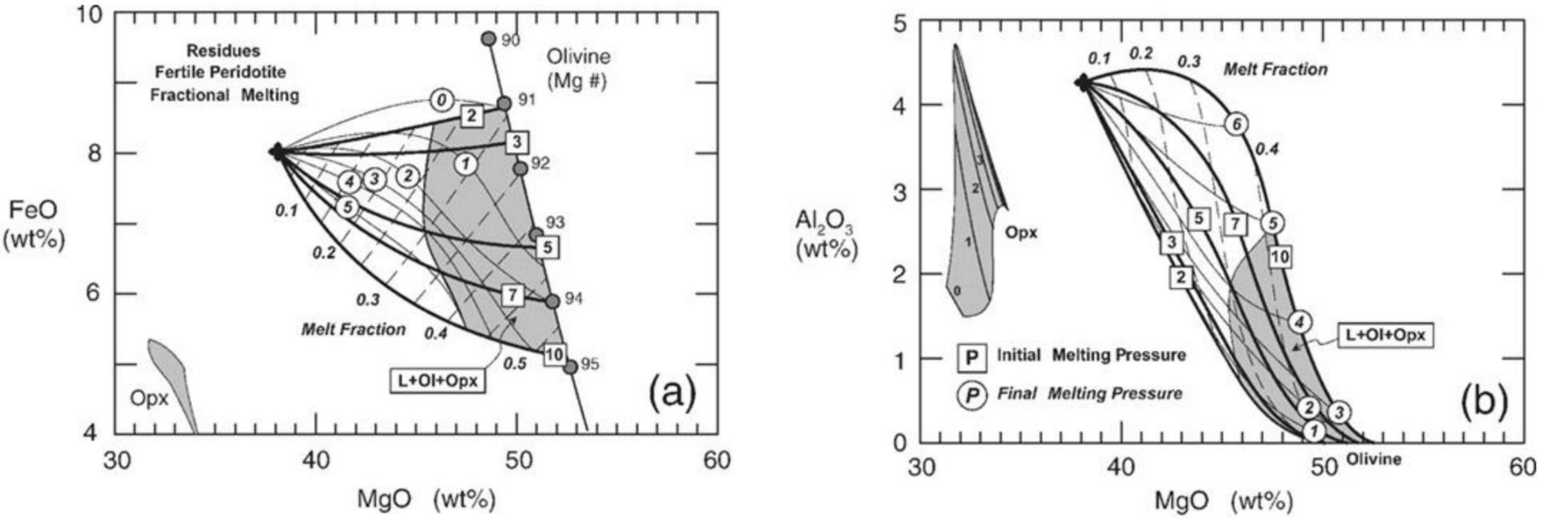
High Pressure
ol unstable; opx produced
10 ol + 75 cpx + 15 gt = 90 liq + 10 opx

Walter, 2014



Partial melting

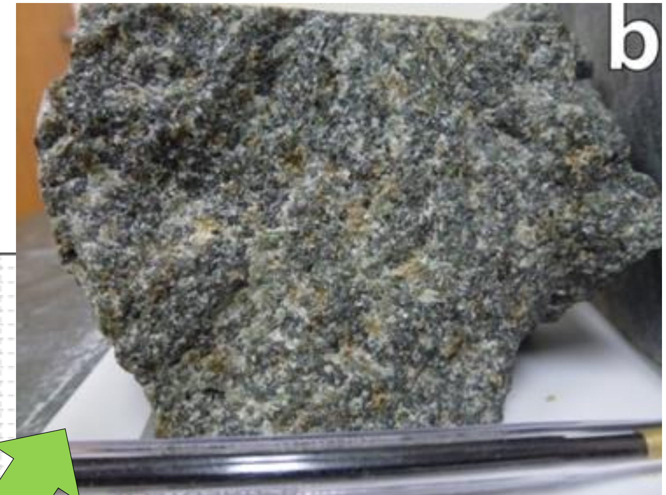
Herzberg, 2004

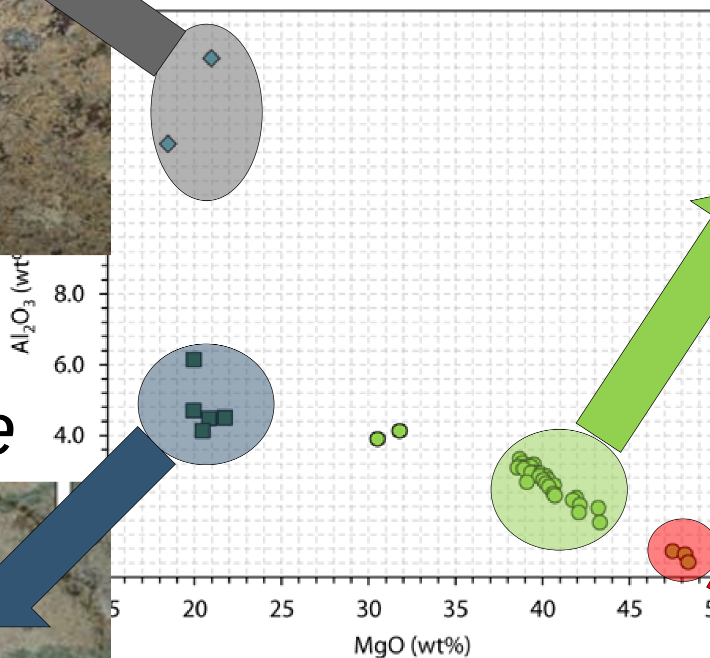


Compositions of peridotites are a function of depth and degree of melting

Pyroxenites

Peridotites



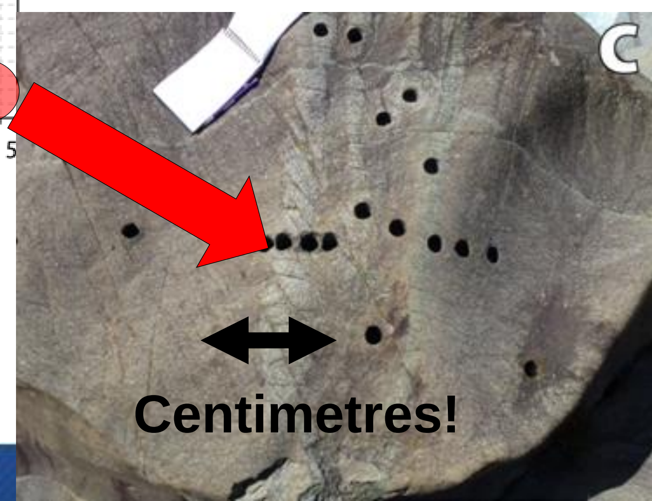


Al-Augite

Lherzolite

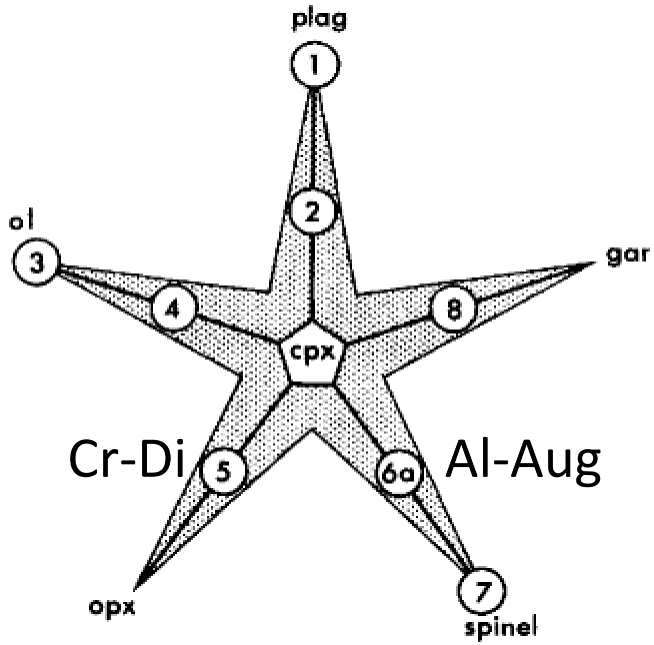
Chrome-Diopside

Dunite



Centimetres!

Occurrence of Pyroxenite



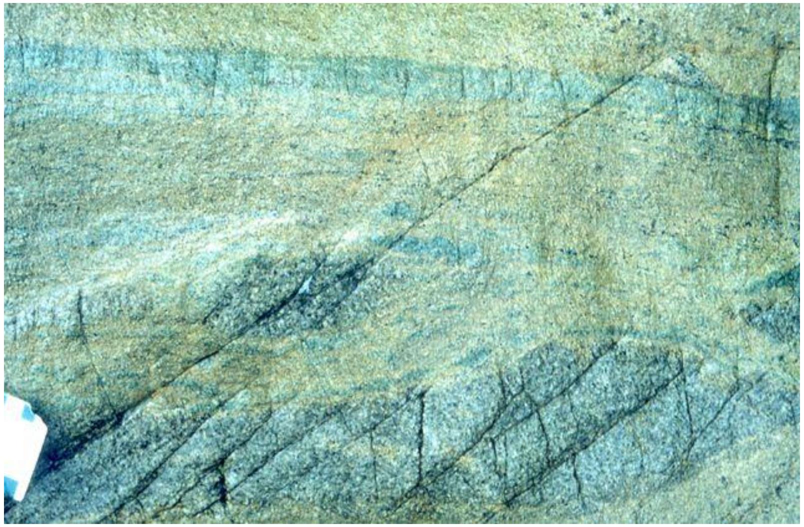
Most fall into two groups:

1. *Chrome Diopside*
2. *Aluminous Augite*

Represent ≈5% of outcrop in alpine peridotites (Ivrea, Beni Bousera, Ronda, etc.) & in spinel xenoliths in alkali basalts (e.g. Irving, 1980)

Suggests a global process

Chrome-Diopside

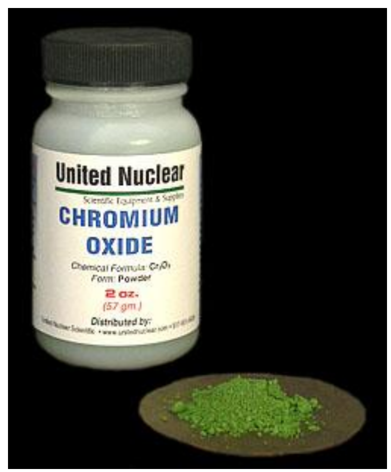


- Earliest event at Balmuccia; mostly concordant with foliation
  - Largely 2/3 diopside, 1/3 orthopyroxene
- Fully equilibrated with surrounding peridotite, often adjacent to dunite
- Bulk rock Cr-Di bands are **chemically** and **isotopically indistinguishable** from clinopyroxene in peridotite (e.g. Rivalenti et al., 1995)

What is the significance of the ubiquity of Cr-Di segregations?

How do these rocks contribute to chemical heterogeneity in the upper mantle?

A hint lies in their name…

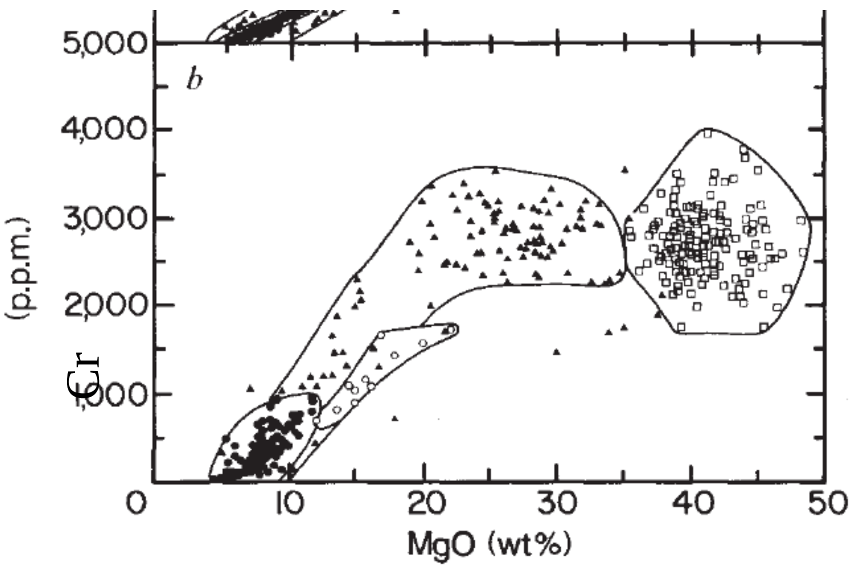


The chromium quandary

Evidence from chromium abundances in mantle rocks for extraction of picrite and komatiite melts

Y. Liang* & D. Elthon†

* Department of Geophysical Sciences, University of Chicago, Chicago, Illinois 60637, USA
† Department of Chemistry, University of Houston, Houston, Texas 77204-5641, USA

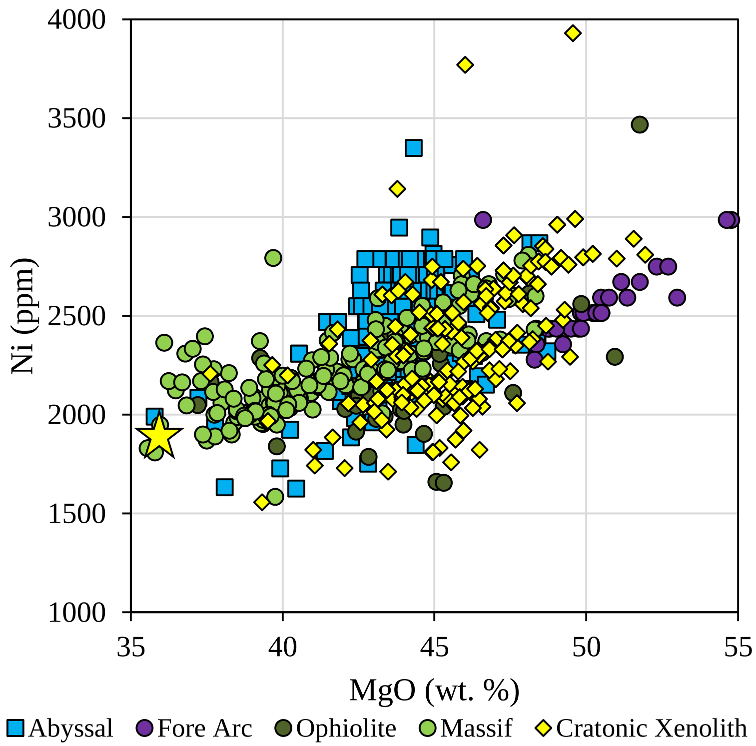


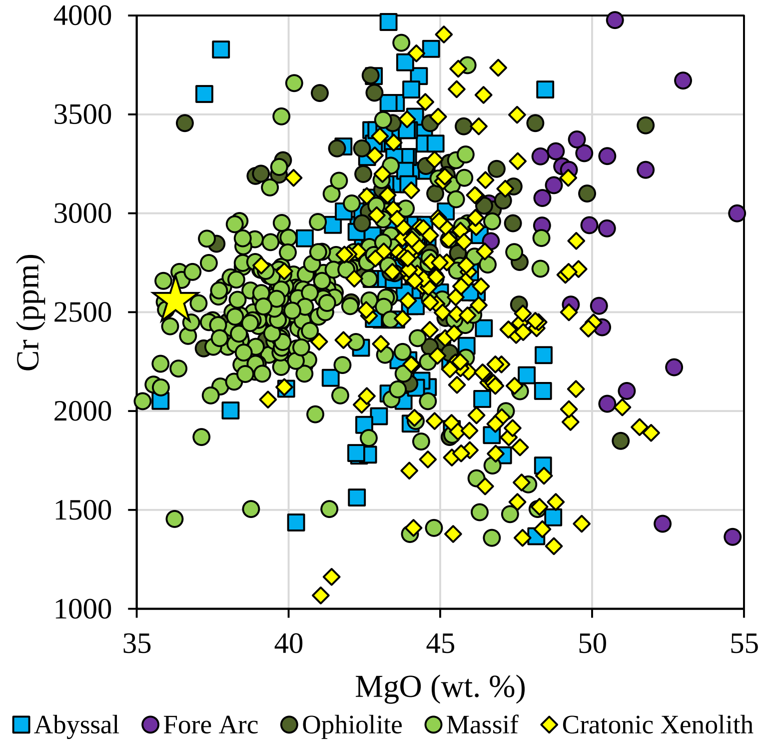
Liang and Elthon in **1990** noted constancy of Cr abundances in peridotites with varying MgO contents

They argued that $D_{Cr} \approx 1$ could only be explained by the extraction of high-Mg melts (komatiites, picrites).

The chromium quandary

This tendency holds for a much larger dataset of global peridotites

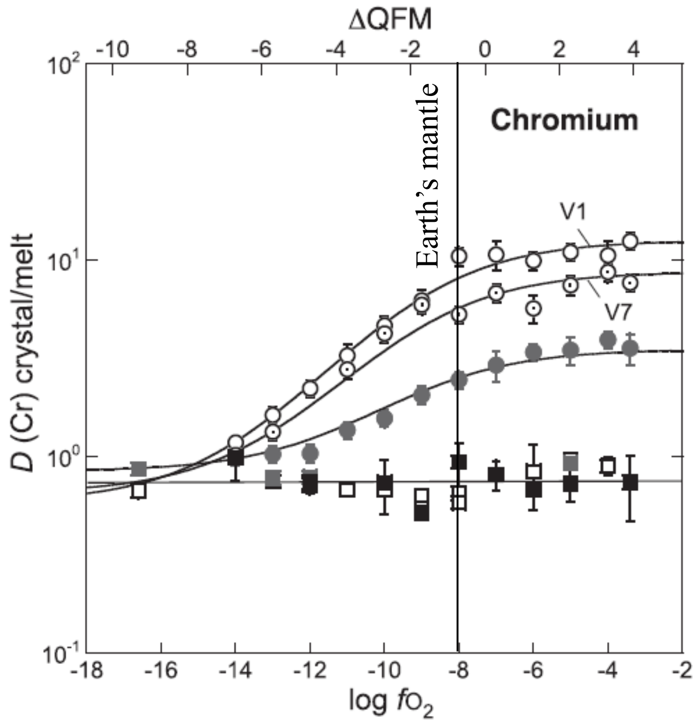




Compiled from Canil (2004)

The chromium quandary

Chromium Mantle-Melt Partitioning



Clinopyroxene

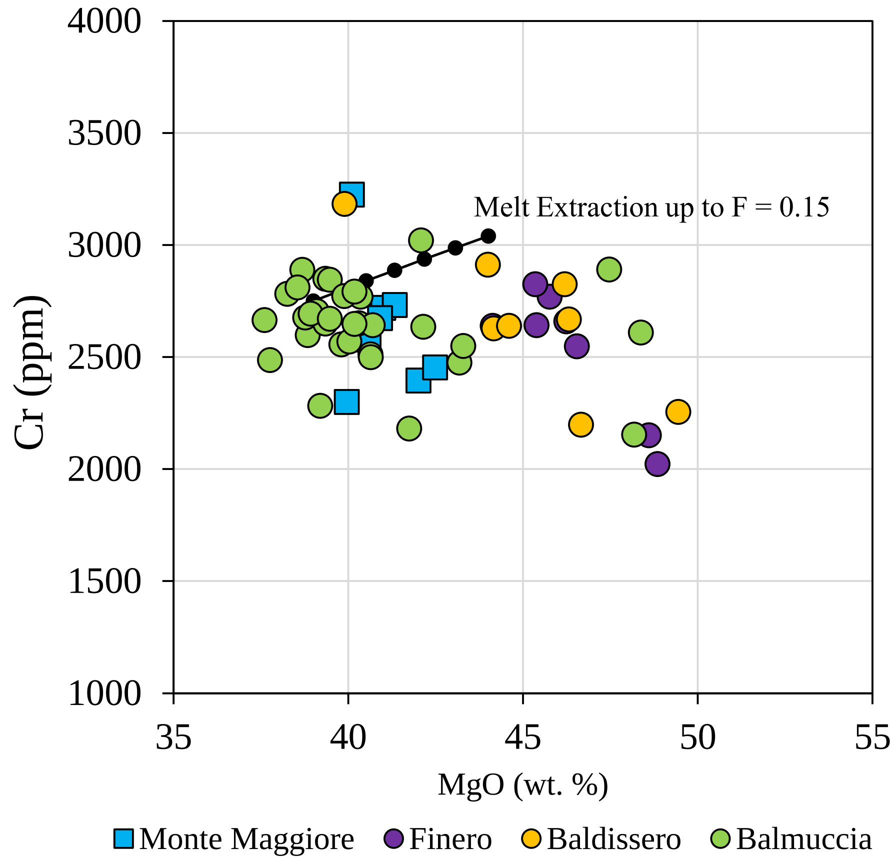
Orthopyroxene

Olivine

Mallmann and O'Neill, 2009

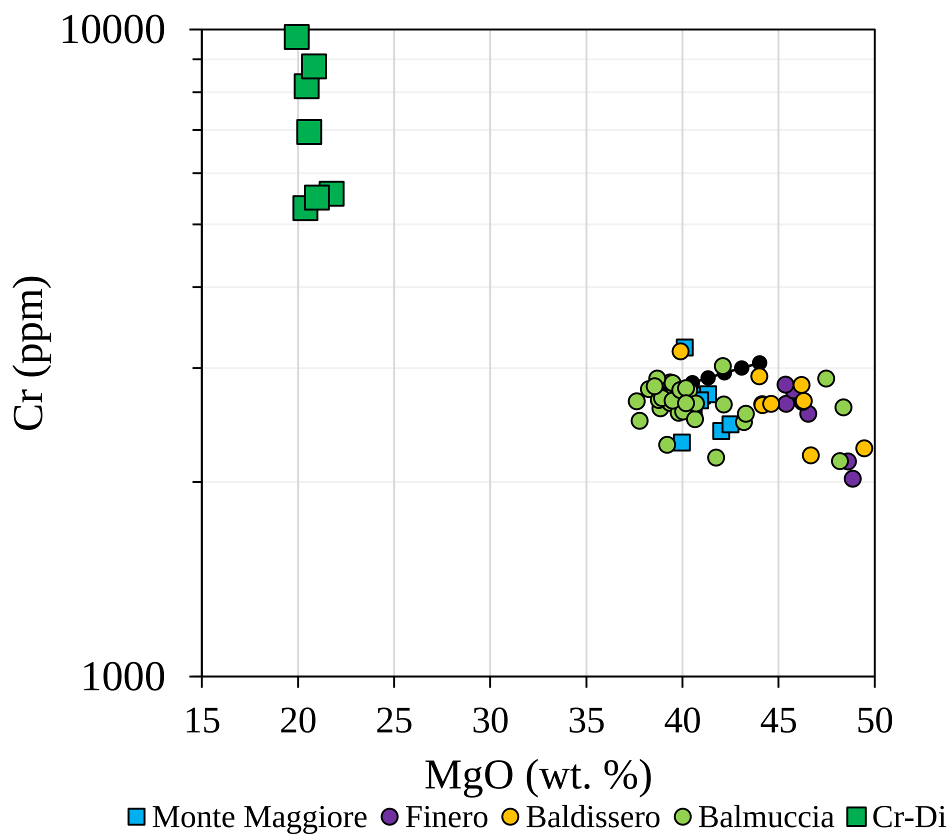
$$\text{Bulk } D_{Cr(3+)}^{\text{Mantle-Melt}} \approx 3$$

The chromium quandary



Partial melting under normal mantle conditions cannot reproduce the trend in massif (or global) peridotites

The chromium quandary



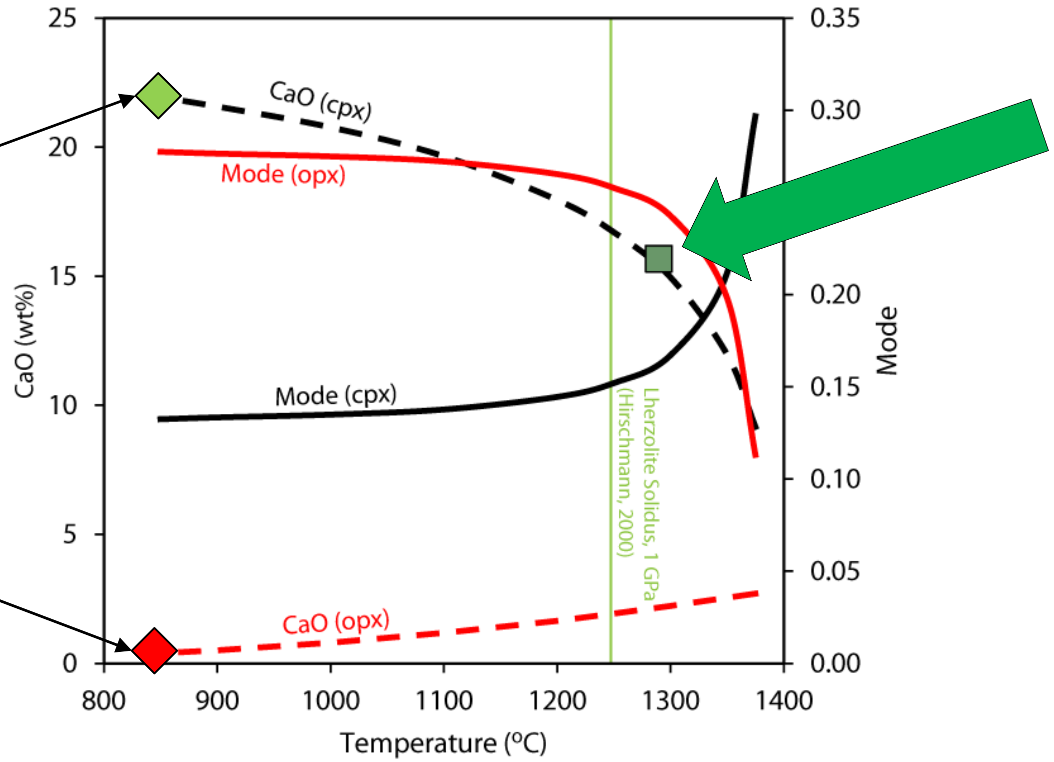
The only lithology in the upper mantle with more Cr together with lower MgO than in lherzolites are the **Cr-Di** websterites

The role of chrome diopside

Peridotites are metamorphic rocks => phases change in composition with P and T

Equilibration temperatures are ≈ **850° C** (cf. Brey and Köhler, 1990)

Composition of pyroxenes in lherzolite



Bulk composition of Cr-Di veins

Cr-Di veins derived from parent lherzolite

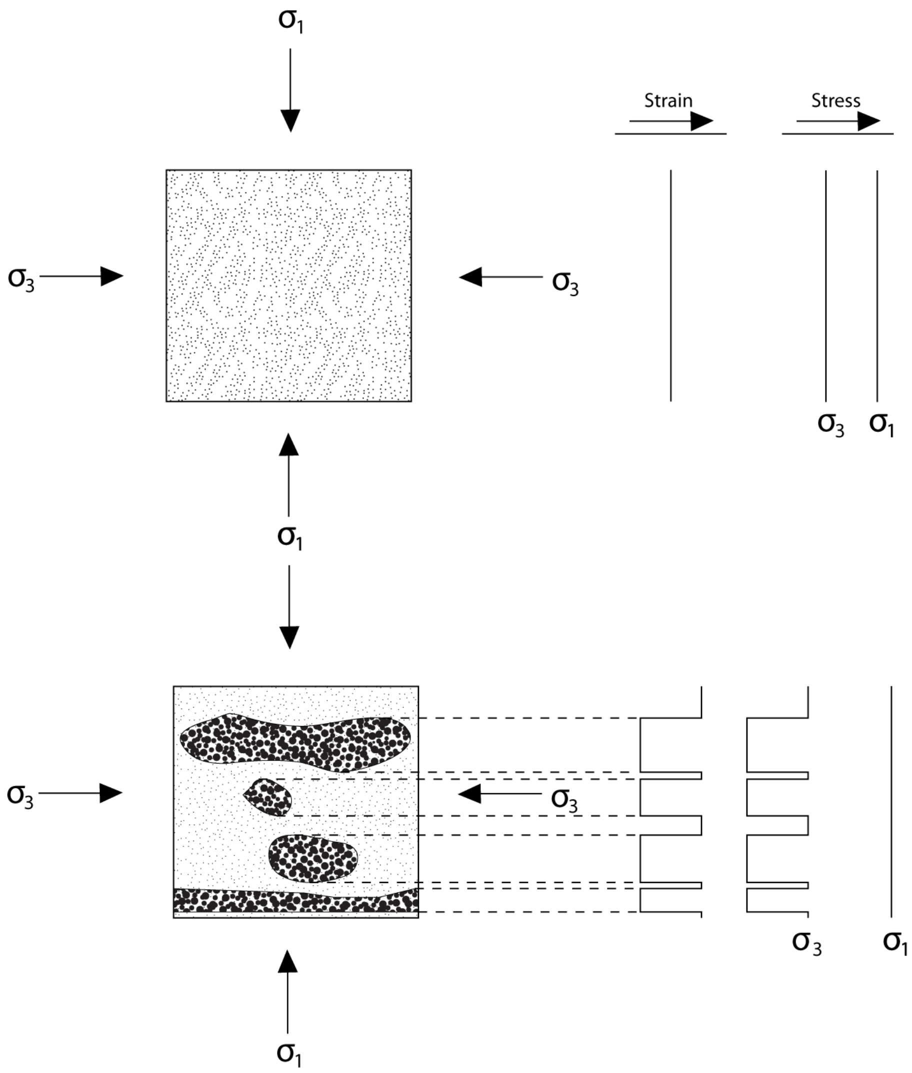
The role of chrome diopside

Local Transport

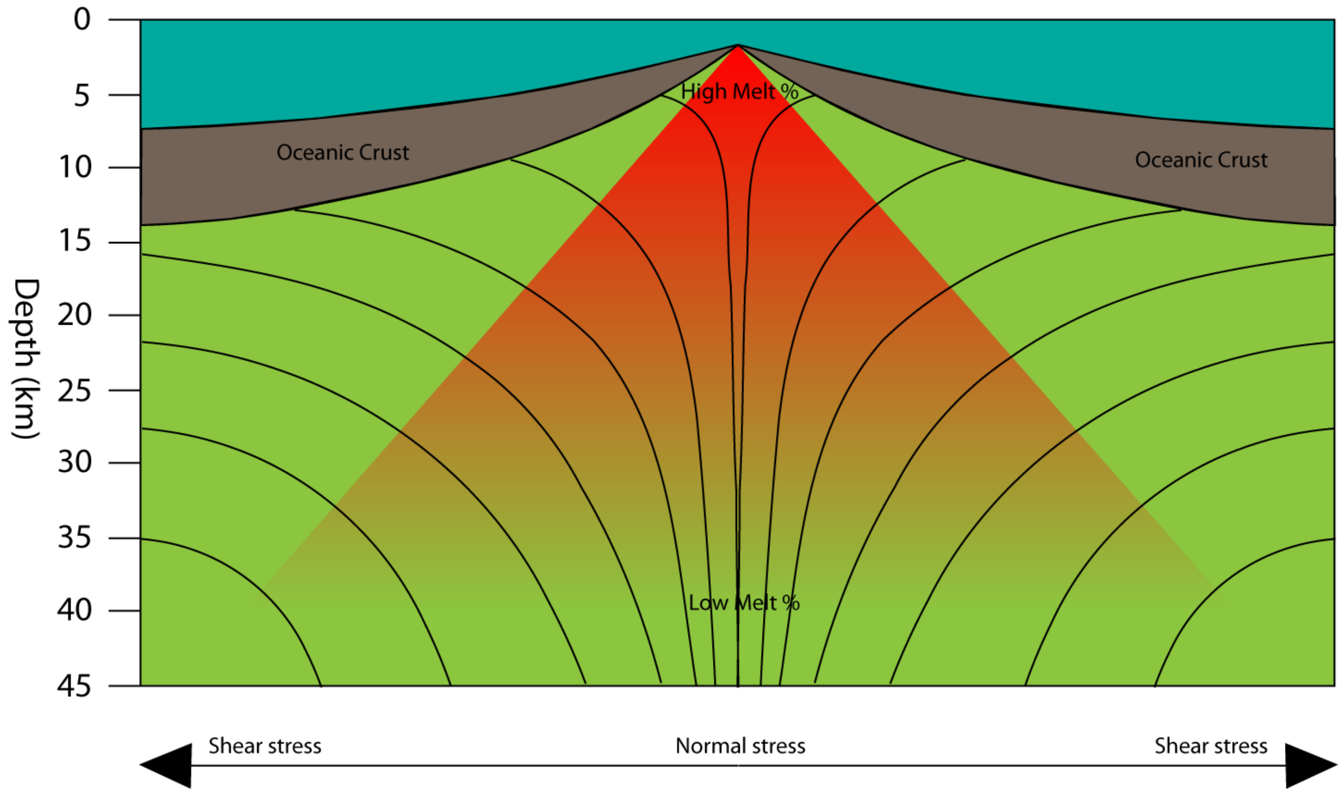
- Adjacent to clinopyroxene-poor peridotite
- Have identical compositions (chemical & isotopic)

Mechanism

- Melt focusing and dissolution / reprecipitation (Dick and Sinton, 1979), melts re-precipitate new pyroxene pressure shadow
- Clinopyroxene undergoes pressure solution because it is i) more competent and ii) has lower solidus T than olivine or opx

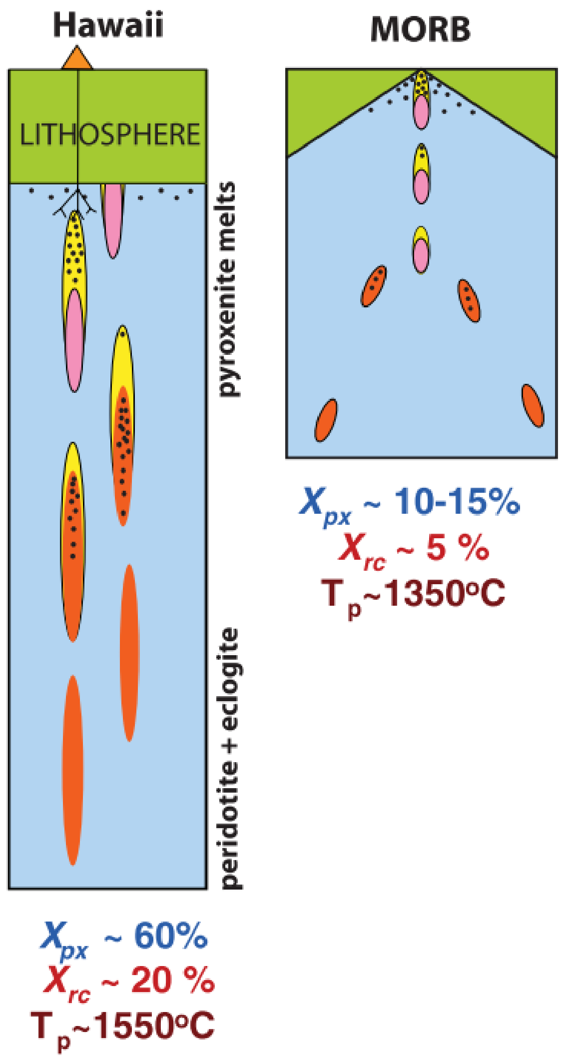


Chemical variability in the mantle



- Pressure solution is favoured under high deviatoric stress
- Ascending mantle experiences shear stress at base of lithosphere
- Explains widespread occurrence of pyroxenites

Plumes and melting



Sobolev et al. (2007)

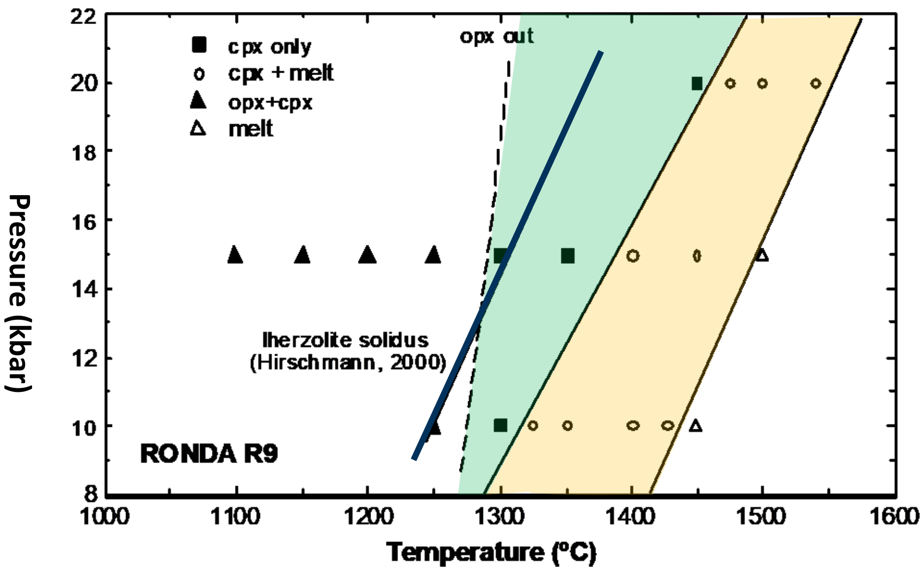
- Proportion of pyroxenite in sources of oceanic basalts (MORB & OIB) is not well known – inferred assuming a common ‘pyroxenite’ composition

- Differences in source composition affect the inferred mantle potential temperatures deduced from petrological evidence (*e.g.*, MgO content of basalts)

Experiments on pyroxenites

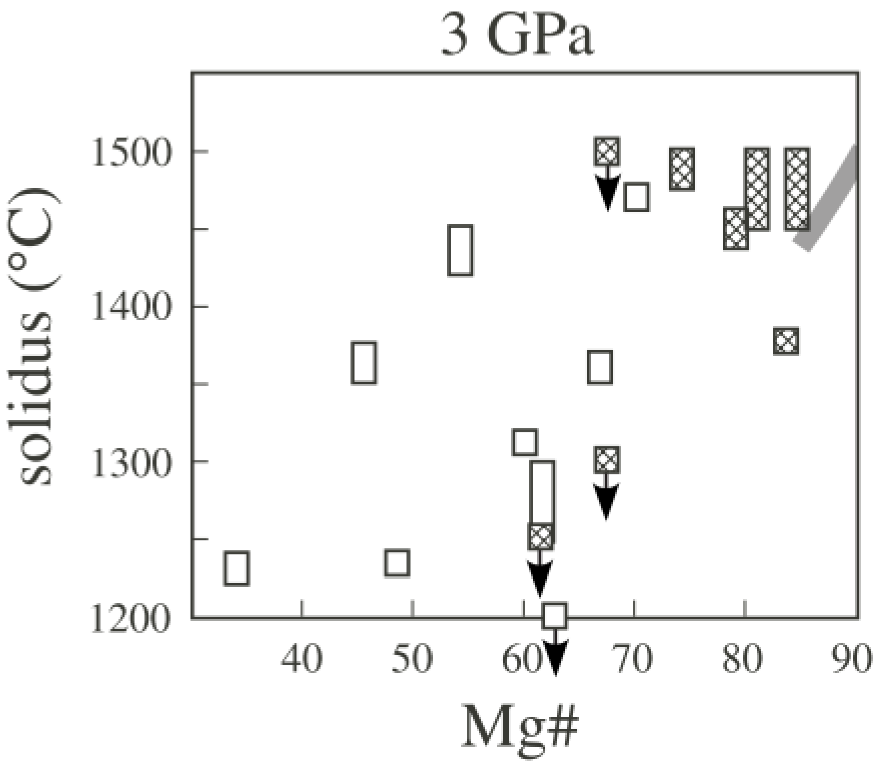
- Cr-Di veins are **single-phase** clinopyroxene at mantle *T* and *P*
- Solidus temperature is **75° C** higher than peridotite at 1.5 GPa

	R9	B2
	Ronda	Balmuccia
	websterite	sp-websterite
SiO_2	52.57	51.13
TiO_2	0.06	0.25
Al_2O_3	3.78	4.67
Cr_2O_3	1.13	1.3
FeO	4.07	5.07
MgO	21.13	21.39
CaO	16.05	14.27
Na_2O	0.36	0.66
K_2O	0.005	0.008
P_2O_5	<.002	0.021
SO_3	0.04	0.31



- Peridotite would melt before any newly-formed Cr-Di regions

Pyroxenite compositions



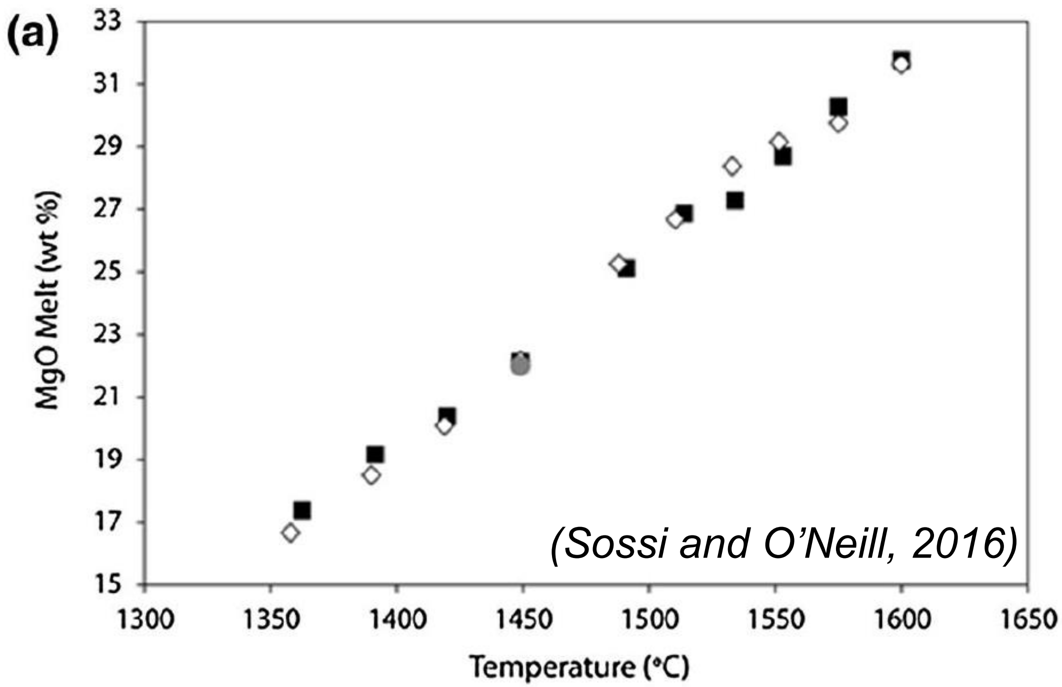
Kogiso et al., 2004

- Large compositional variability in mantle pyroxenites
- Solidus temperature is proportional to their Mg# (not captured in CMAS projections)
- May not necessarily enhance partial melting rates in upwelling mantle (Kogiso et al., 2004; Lambart et al., 2014)

MgO contents and eruption temperatures

How do we break the degeneracy between **composition** and **temperature?**

Experiments show MgO (wt. %) of a silicate melt is related to 1 atm liquidus temperature



T (1 atm, ° C) = 1091+16*MgO (wt. %)

Mantle potential temperature

The **mantle potential temperature** (T_p) is the temperature a parcel of mantle peridotite would have at the surface if it were to adiabatically decompress without melting:

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{T\alpha}{\rho C_P}$$

Taking into account the latent heat of fusion and the positive dP/dT slope of magmatic liquids:

$$T_p = T_{at\ P} + F\frac{\Delta H_{fus}}{C_P} - \frac{T_{at\ P}\alpha}{\rho C_P}\partial P$$

Where the expression may broadly simplify to:

$$T_{liq} \approx \frac{4}{5}T_p$$

Can relate eruption temperatures to mantle temperatures

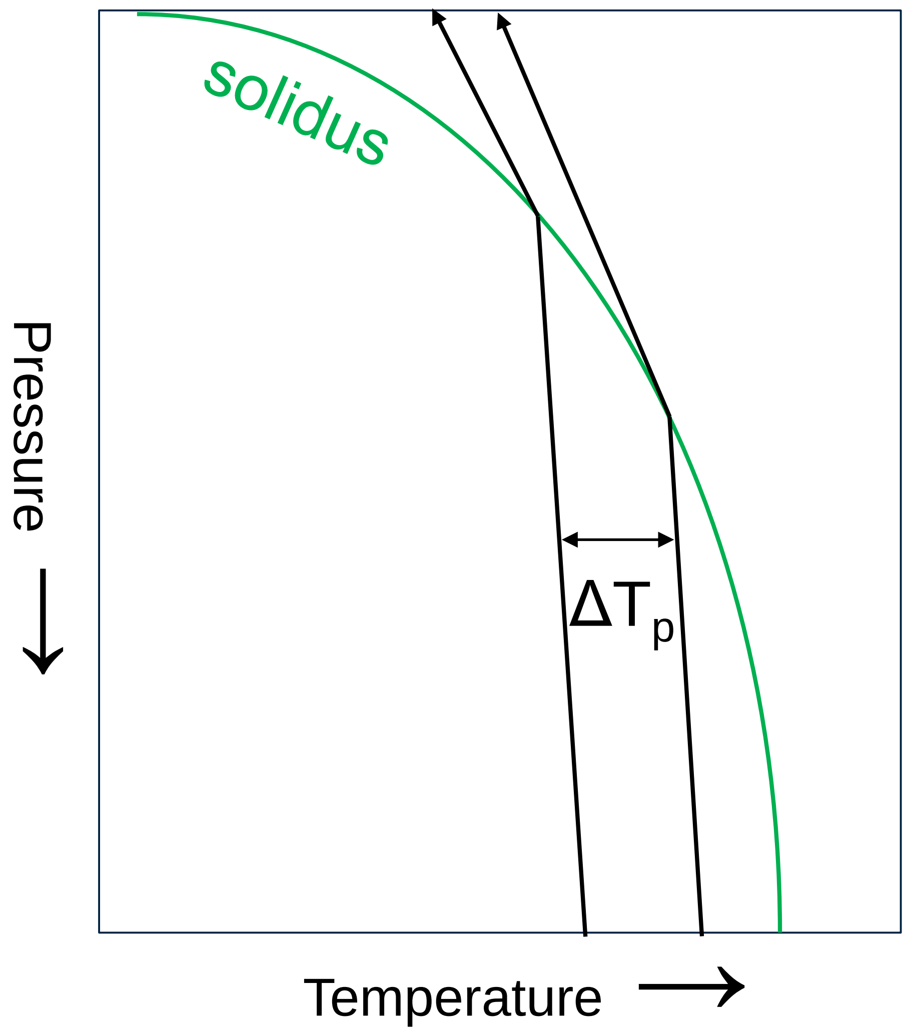
(*e.g.* McKenzie & Bickle, 1988; PRIMELT, Herzberg & Asimow)

Factors affecting T_p

Inherent in the calculation of T_p from MgO content is the assumption of a common:

a) Degree of melting

Can be explicitly accounted for (see above; Herzberg and Asimow, 2008), but not always done

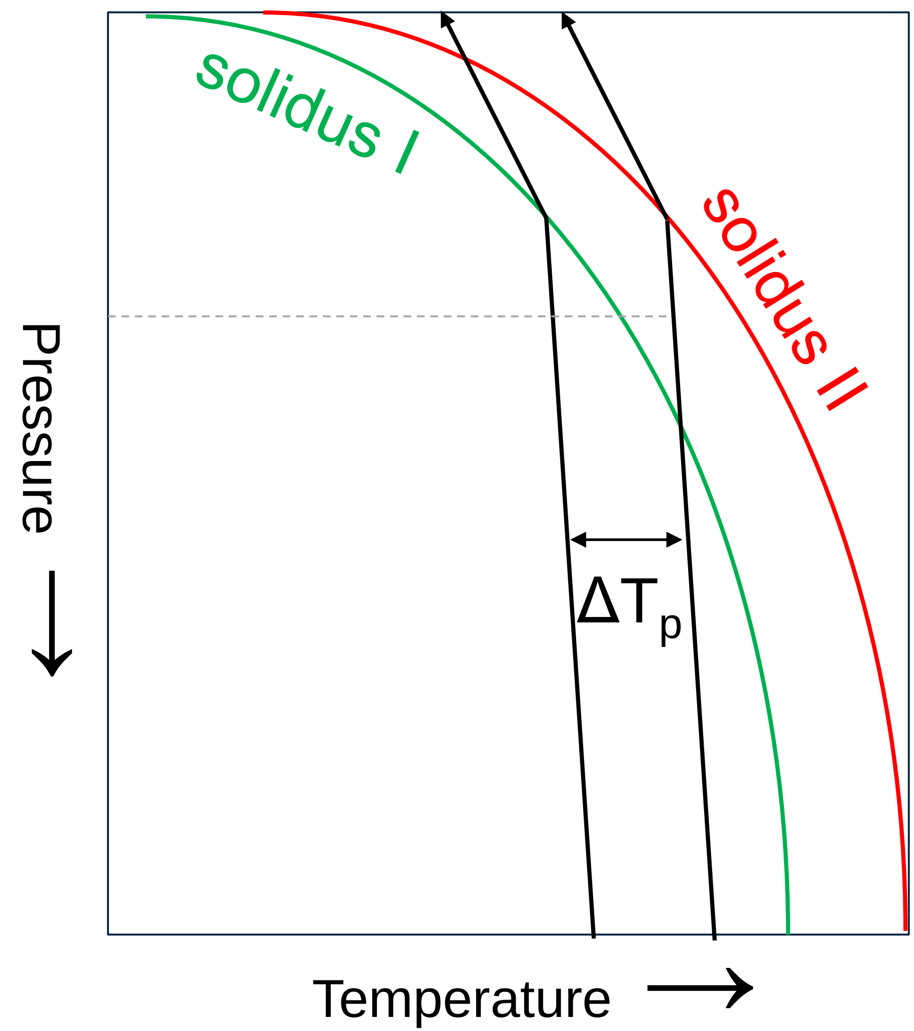


Factors affecting T_p

Inherent in the calculation of T_p from MgO content is the assumption of a common:

b) Source composition

In order to achieve the same degree of melting at a given P, which controls MgO content, T_p must be higher for a more depleted source

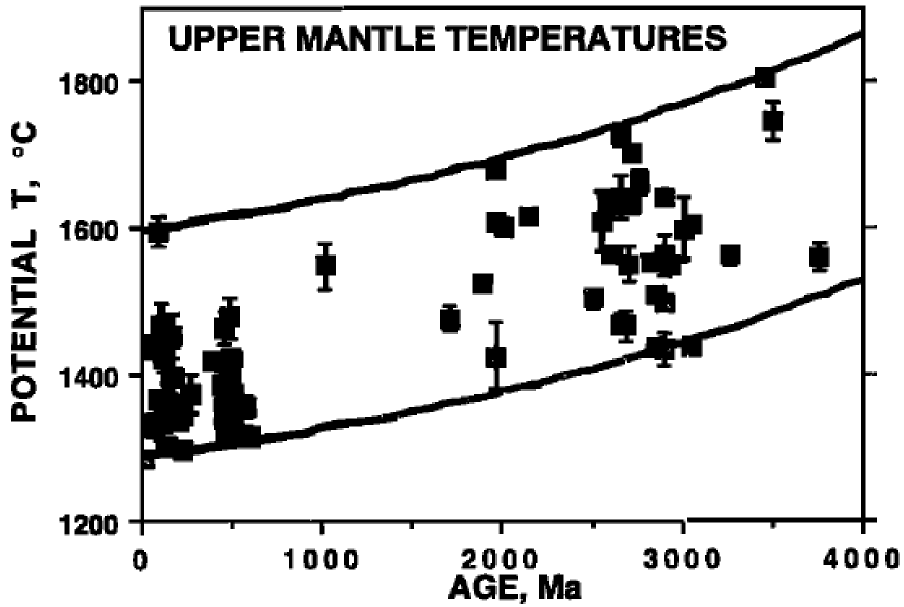


Mantle temperatures through time

MgO in basalts, **ΔT_p = 150-200°C** from modern to Archean is predicted (Abbott et al., 1994; Campbell and Jarvis, 1984; Herzberg et al., 2010).

Models predict little or no increase in temperature during the Archean

Abbott et al. (1994)

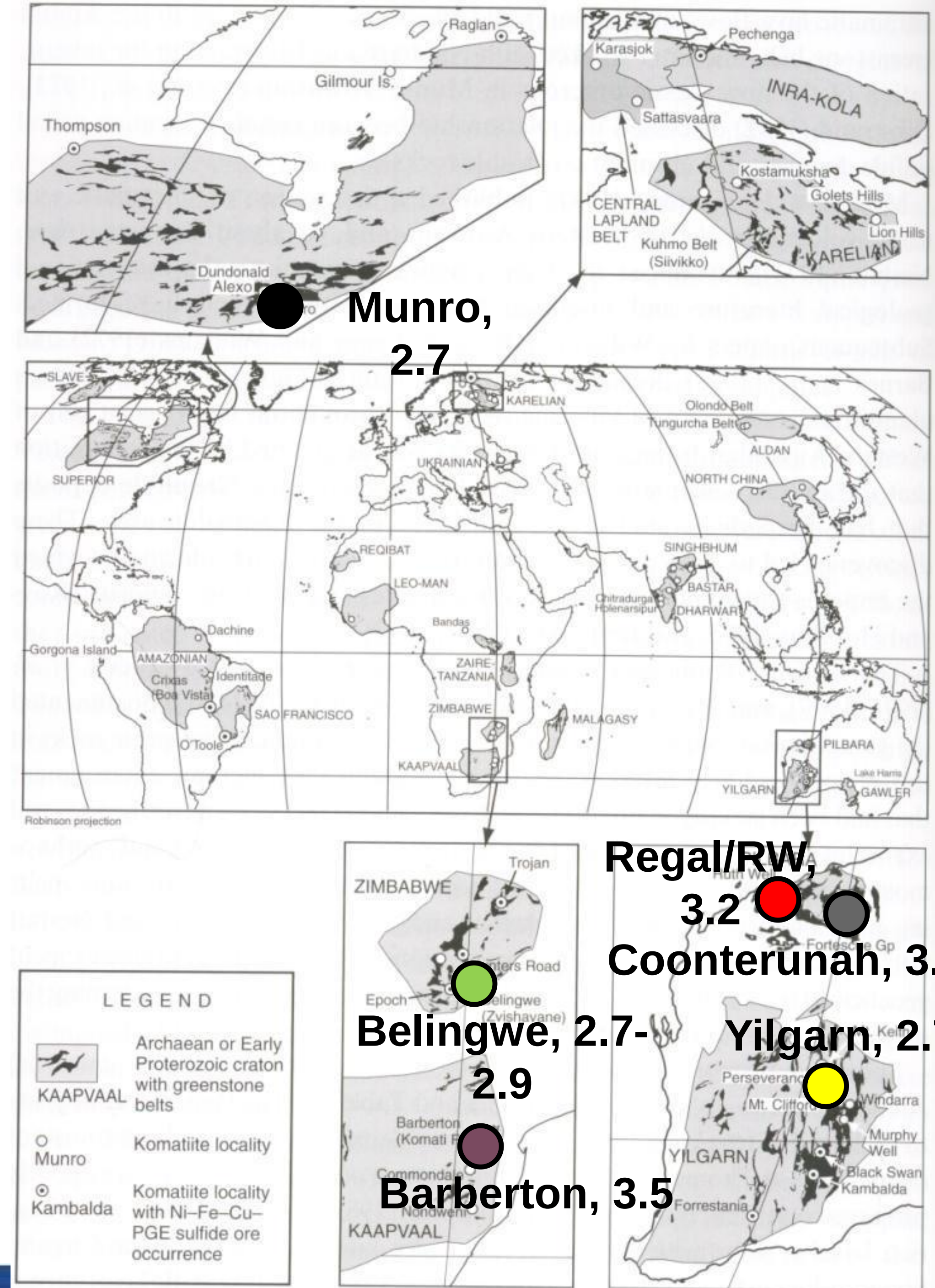


ΔT_p = 150-200°C

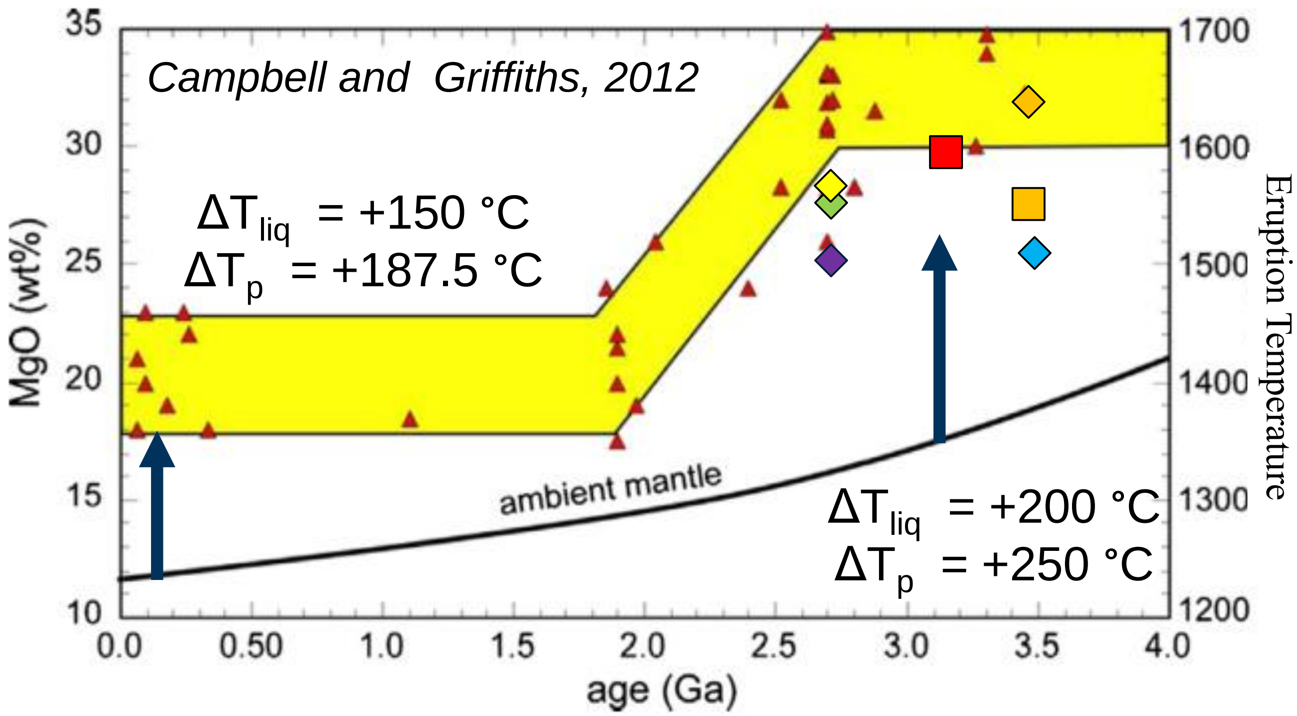
Other evidence for increasing temperatures?

Komatiites

- Formed in Archean plumes
  - Have > 18 wt% MgO (>1400°C T_{liq})
- High degree partial melts (25 – 40 %)
- High pressures (5 – 9 GPa)
  - Occur as ADK (garnet-bearing sources) or AUK (garnet-free sources)



Mantle temperatures through time



Plume temperatures appear hotter relative to ambient mantle

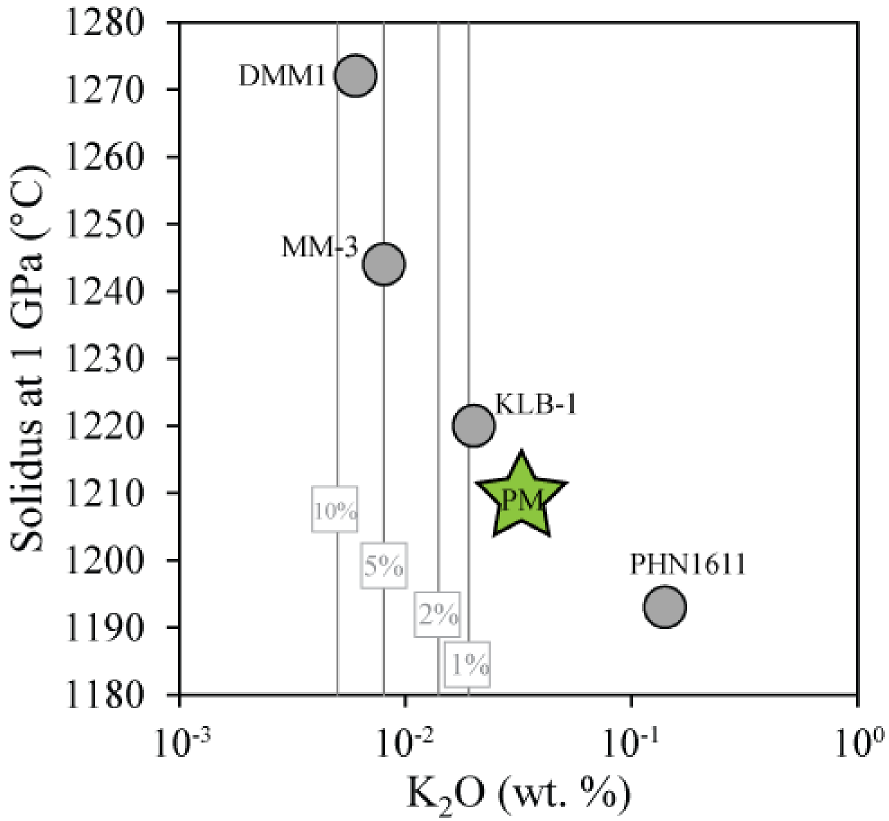
Solidus Temperatures

Composition effect on peridotite solidi

- Incompatible elements decrease solidus T proportional to 1/D **'cryoscopic'** expression (Carmichael, 1974; Hirschmann, 2000)

- Difference of **≈50°C** between DMM and PM

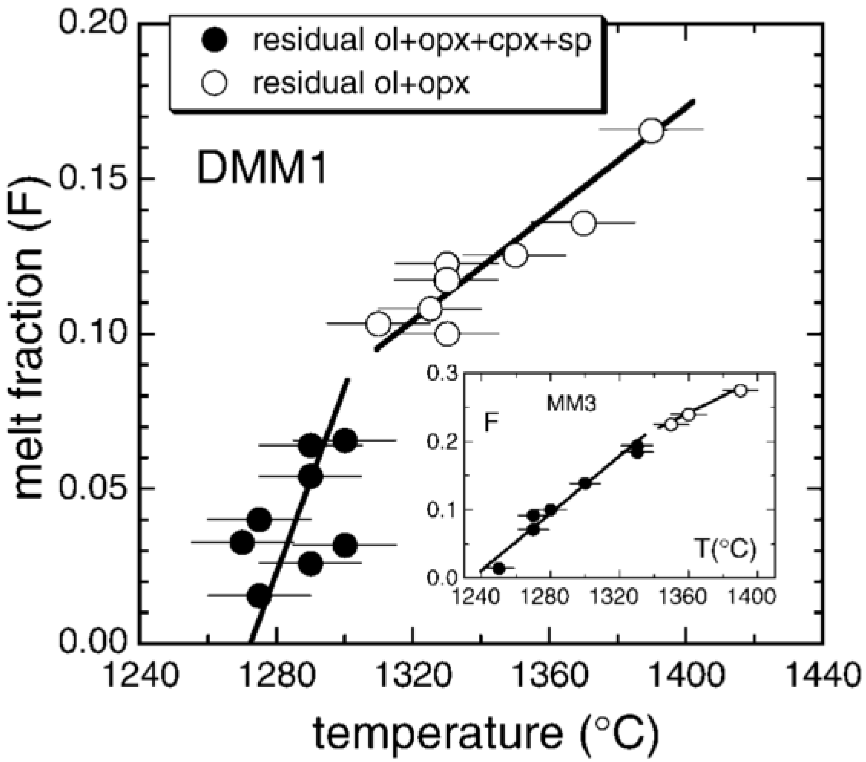
*Assumption of a common source may overestimate T_p increases by 50°C**



Grey circles = experimentally-determined peridotite solidi
Grey lines = fraction of melt extraction from PM

*This is within uncertainty of T_p calculations, 70-90°C (cf. Herzberg and O'Hara, 2002)

Melt productivity



Wasylenki et al., 2003

Phase exhaustion (cpx-out) decreases productivity; i.e., $(dF/dT)_P \downarrow$ (Asimow et al., 1997)

Requires more energy per melt increment

Occurs earlier in more depleted compositions (Wasylenki et al., 2003)

Source Depletion

Evidence of source depletion in the mantle?

The Rare Earth Elements (REE) useful for modelling partial melting

At high F, ratios of incompatible elements are equal to that in source;

If $D_A \approx D_B = 0$, then their abundance α 1/F, and $(C_A/C_B)_{(l)}$ is constant

Batch melting

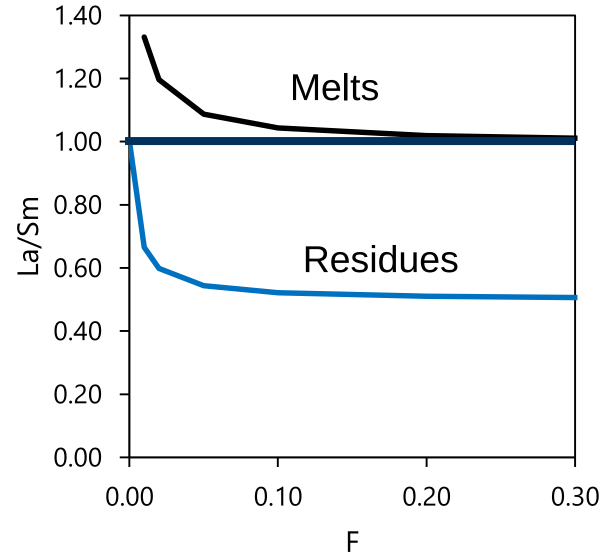
Conc. in liquid

$$\frac{C_l}{C_o} = \frac{1}{D + F(1-D)}$$

Conc. in source

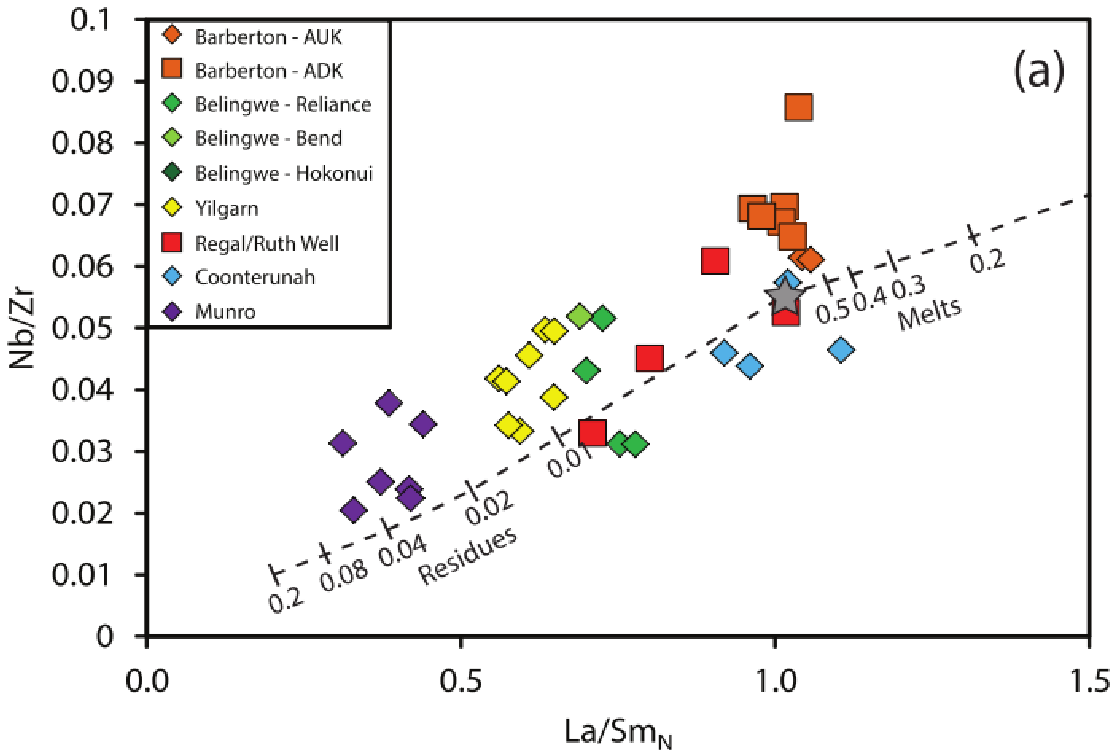
Melt fraction

Partition coefficient



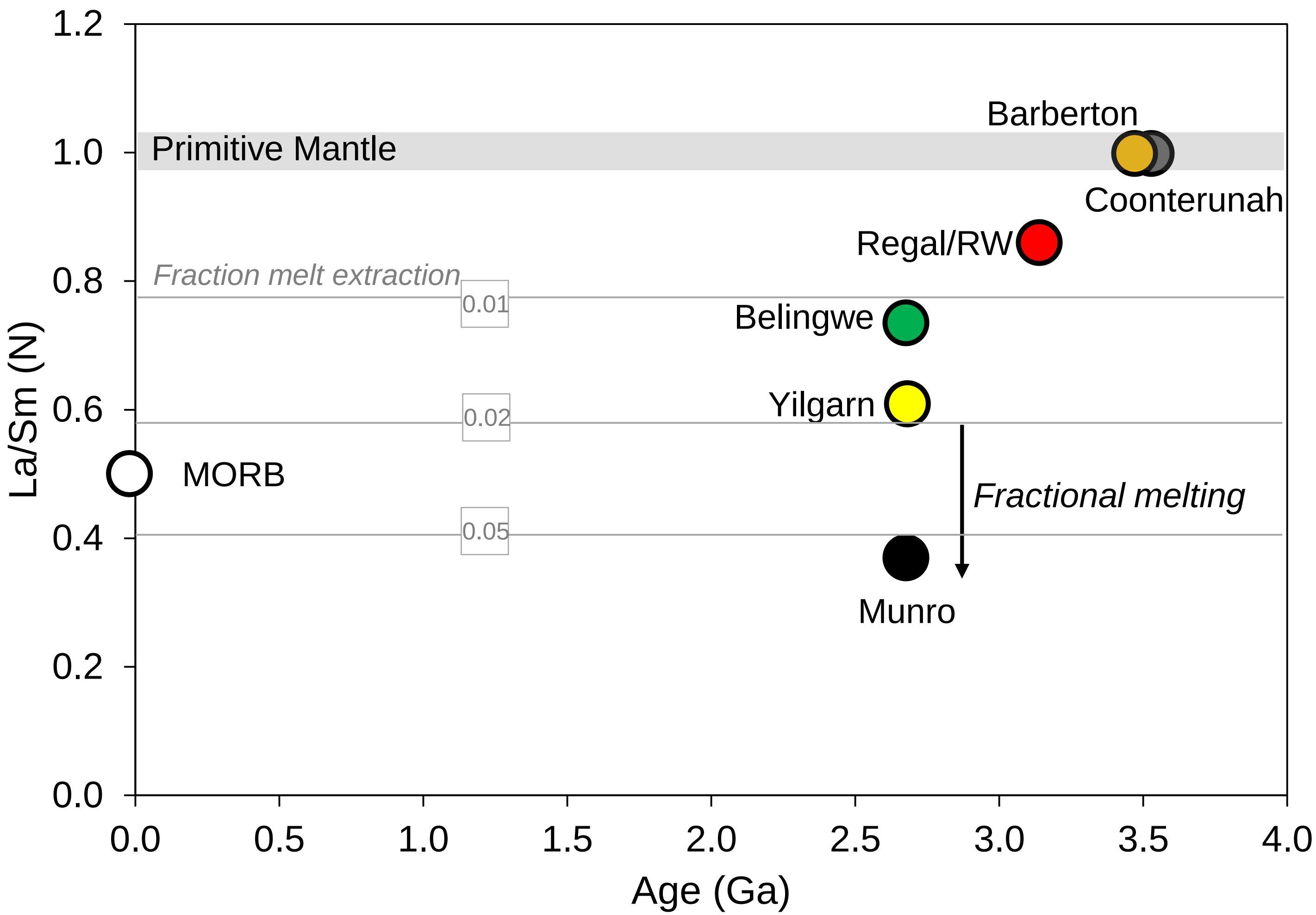
Source Depletion

Examples of element pairs that behave similarly but have different incompatibility are La/Sm and Nb/Zr

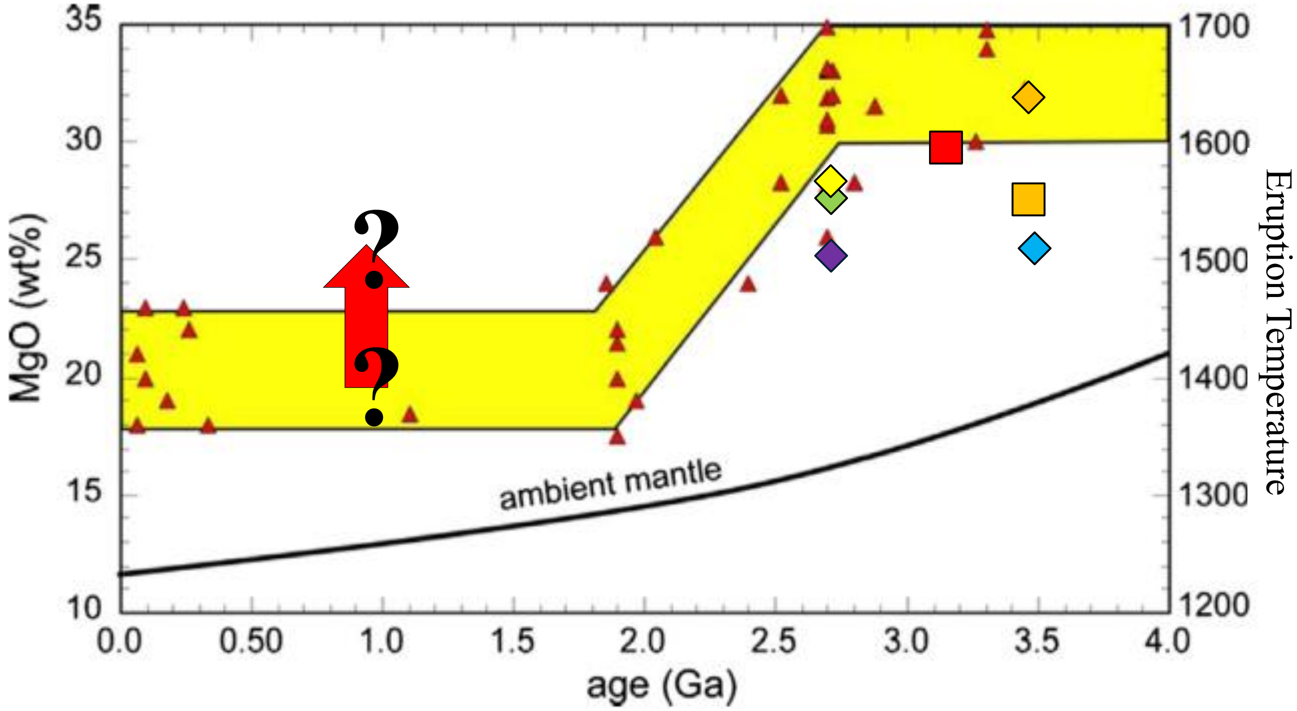


Komatiite sources range from **primitive mantle**-like to small (**5%**) degrees of melt extraction

Secular Mantle Depletion



Archean Mantle Temperatures

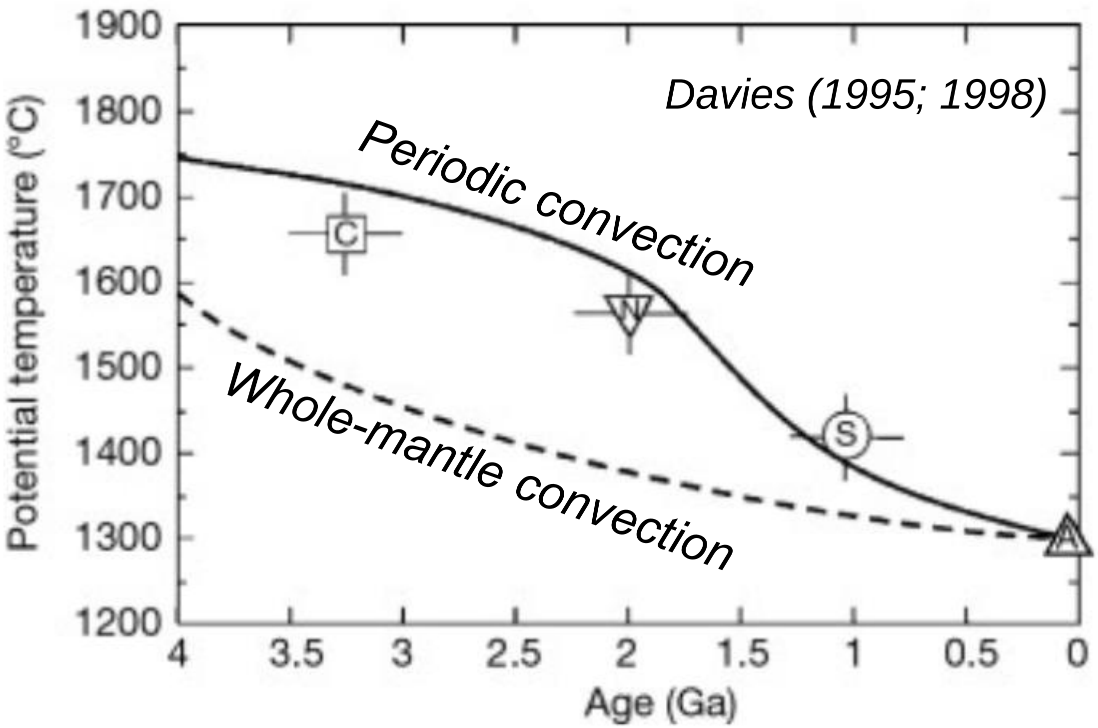


Drop in mantle temperatures not as drastic as currently thought

Requires thermodynamic-numerical models of mantle melting to quantify this effect (cf. Herzberg et al., 2010)

Geodynamic Models

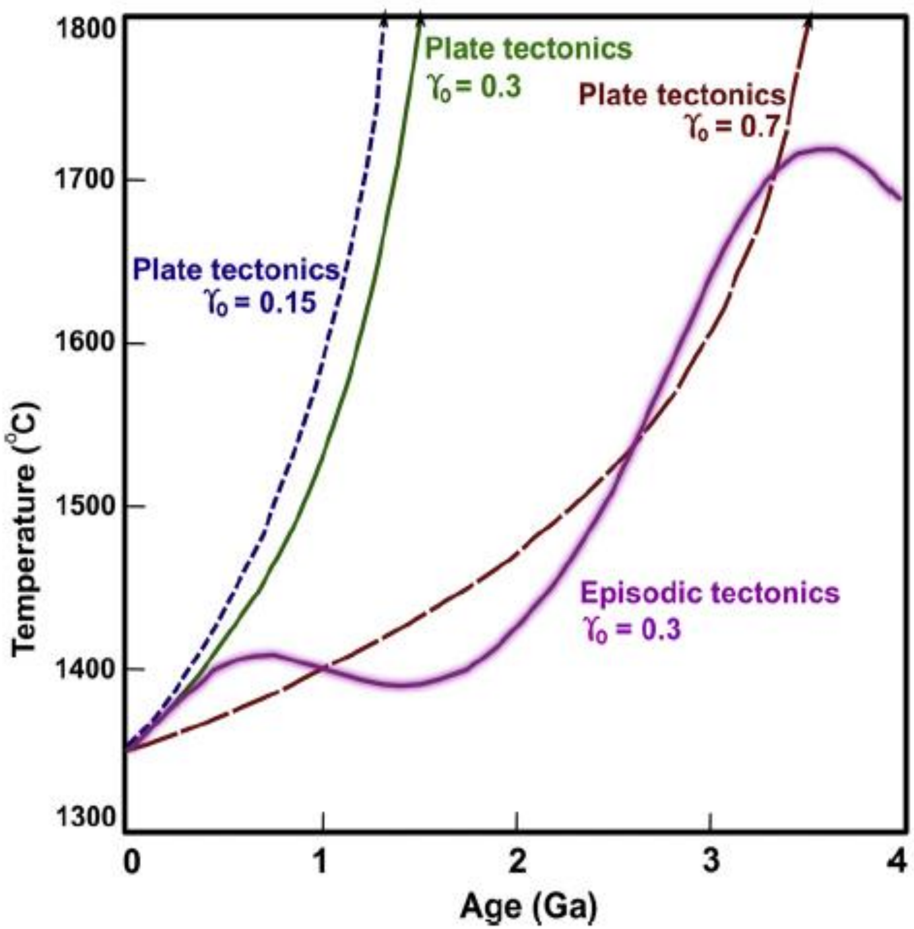
What implications do temperatures have for mantle convection?



Heat production = by radioactive decay; Heat loss = by convection

Archean Dynamics

Silver and Behn, 2008; O'Neill and Debaille, 2014



For reasonable estimates of the Urey ratio, γ, where (Korenaga, 2008):

Heat production

$$\gamma = \frac{H(t)}{Q(t)} \approx 0.3$$

Heat flux

A plate tectonic regime results in an Archean thermal 'catastrophe'

Rather, episodic plate tectonics are required to reduce the amount of heat loss

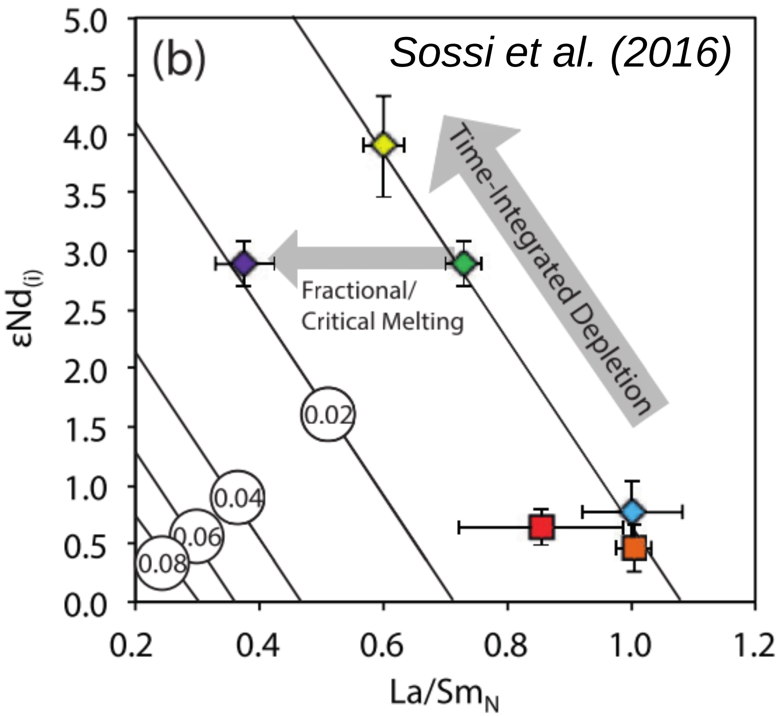
Suggests a vastly different **stagnant-lid** regime

More precise constraints needed for the magnitude of the change in T_p

Timing of Source Depletion

Current thinking:

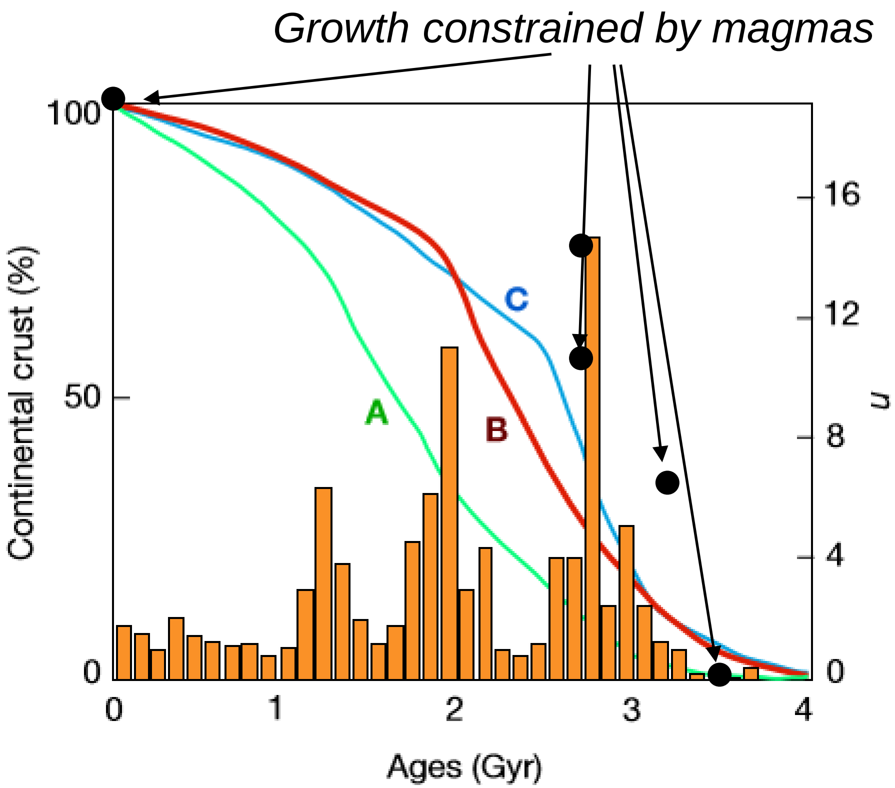
- Plumes come from ‘undepleted’ lower mantle
- La/Sm depletion comes from ‘dynamic’ melting within the plume (Robin-Popieul et al., 2012)



However, the degree of source depletion $(La/Sm)_N$ correlates with the εNd at time of emplacement

Hence melt depletion must have occurred **prior** to plume ascent

Secular Mantle Depletion



Hawkesworth and Kemp, 2006

Models suggest most crustal growth occurred in late Archean/early Proterozoic (e.g. Taylor and McLennan, 1981, curve C)

If the La/Sm_N ratio of komatiites, vs. MORB gives the degree of crust extraction, and the MORB value = 100%, then:

$$X_{Crust} = \frac{((La/Sm)_{PM} - (La/Sm)_{Kom})}{(1 - (La/Sm)_{MORB})}$$

Calculations suggest that 60-75% of the current crust was formed by 2.7 Ga

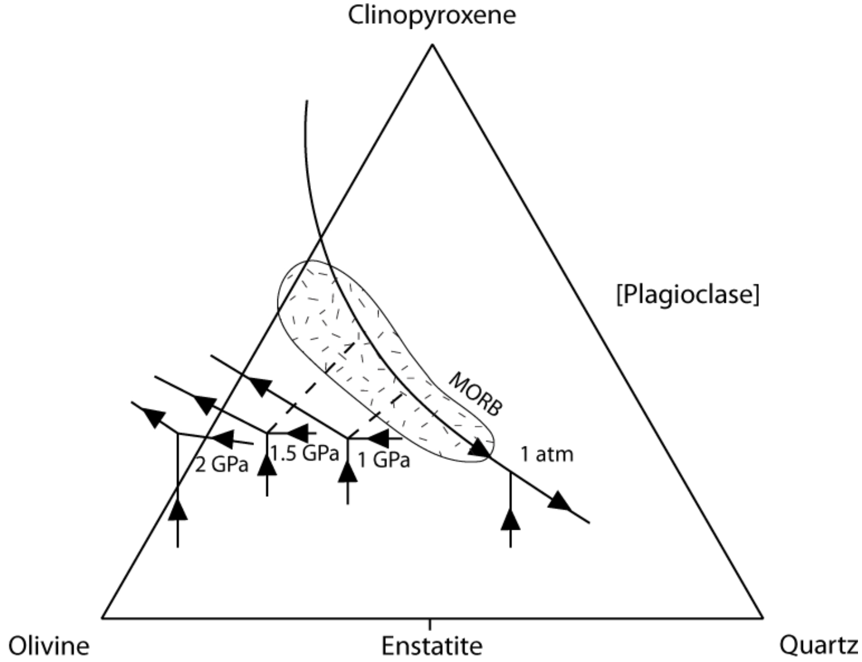
Summary

- The real mantle is strongly heterogeneous
- Formation of Cr-Di pyroxenites are important mantle differentiation processes
- Pyroxenites are not always more fusible than peridotite
- Mantle potential temperature is thus difficult to assess due to the differences in mantle composition
- Secular trend to more depleted magmas with time indicative of crustal growth on Earth

The role of chrome diopside

Cumulates from partial melts?

OPX + CPX ± Sp = Ol + Melt

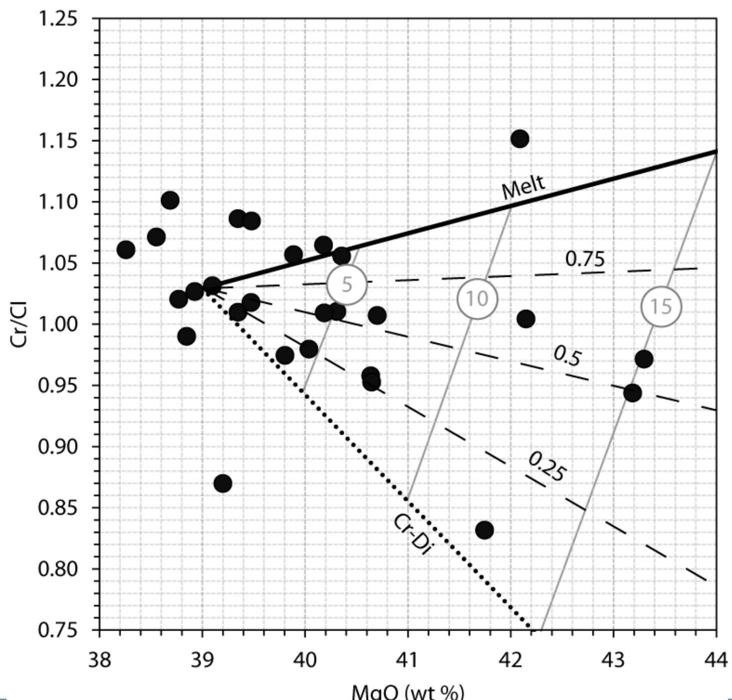


- Not the case for Cr-Di due to expansion of the olivine field at lower P
- Metamorphic textures in Cr-Di and in chemical equilibrium with pristine lherzolite

Chemical variability in the mantle

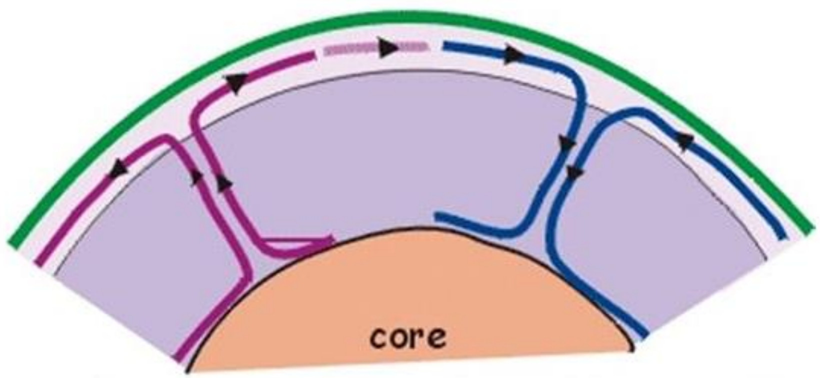
Variability in peridotites can be explained by a combination of…

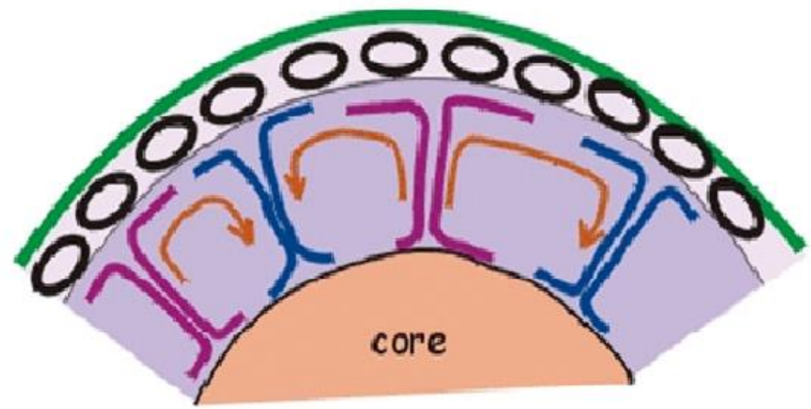
1. Melt extraction
2. Re-distribution of clinopyroxene



Mantle Convection

Archean? ⟷ Post-Proterozoic?





Implies that **whole mantle** convection occurred in the early Earth, when temperatures were high enough that the 660 km discontinuity was not an impediment to plumes or slabs (*cf.* Klein et al., 2017)

As the Earth cooled, transfer between the upper and lower mantle became more **episodic**, punctuated by discrete plume events