

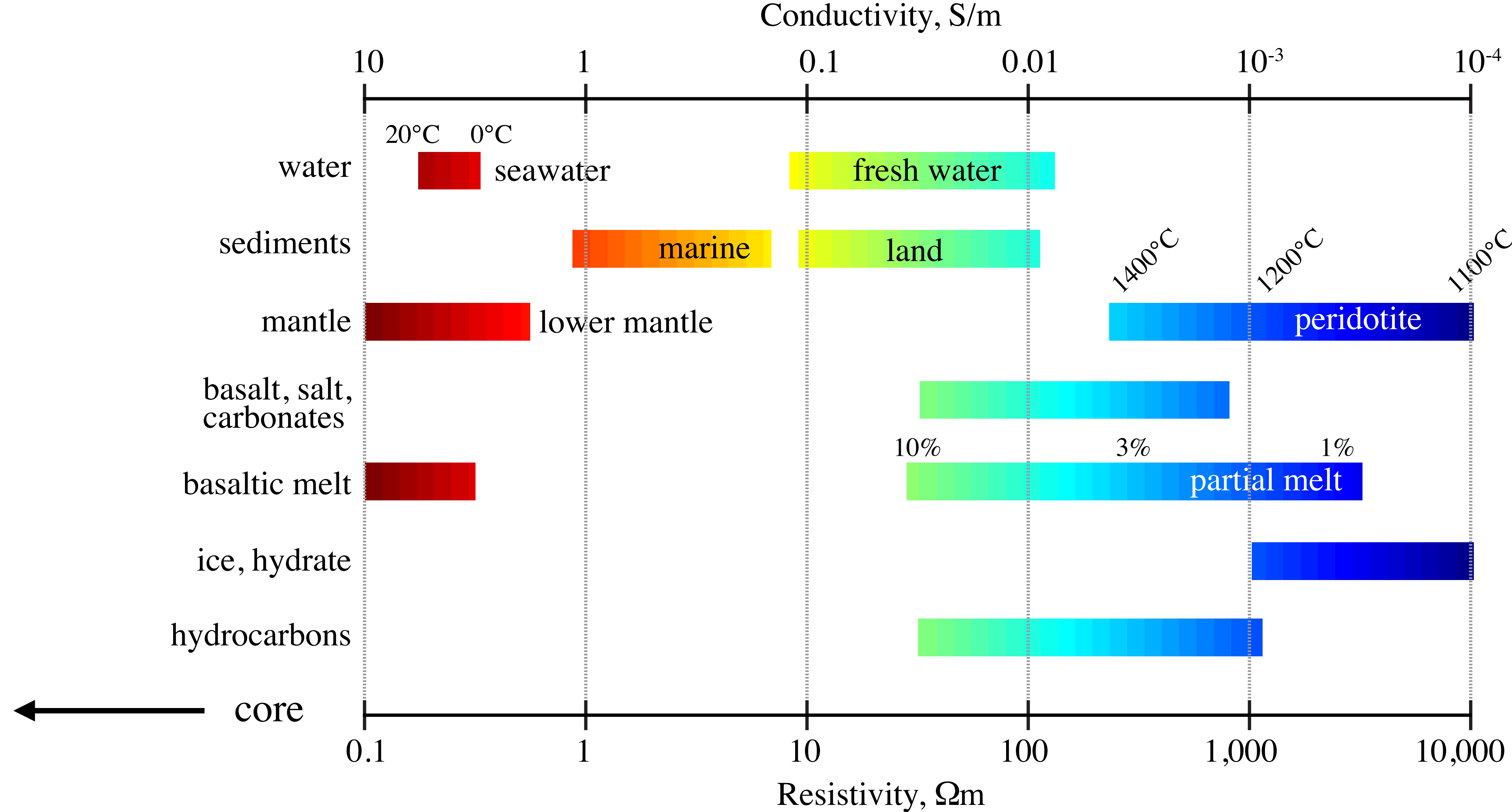
SIOG 231
GEOMAGNETISM AND ELECTROMAGNETISM

Lecture 18

Electrical Conductivity of Rocks, Crust, Mantle, and Core

3/7/2024

Conductivity varies by orders of magnitude:



Ionic conduction:

seawater at 20°C	5 S/m	0.2 Ωm
seawater at 0°C	3 S/m	0.3 Ωm
marine sediments	1 S/m	1 Ωm
land sediments	0.001–0.1 S/m	10–1000 Ωm
igneous rocks	10^{-5} – 10^{-2} S/m	100–100,000 Ωm

Semiconduction and metallic conduction:

Graphite	10,000–1,000,000 S/m	10^{-4} – 10^{-6} Ωm
Galena	10–100,000 S/m	10^{-1} – 10^{-5} Ωm
Pyrite	1–1,000 S/m	10^{-3} –1 Ωm
Magnetite	20,000 S/m	5×10^{-5} Ωm
Copper	5.8×10^7 S/m	1.7×10^{-8} Ωm
Silver	6.2×10^7 S/m	1.6×10^{-8} Ωm
Gold	4.5×10^7 S/m	2.2×10^{-8} Ωm

Defect conduction and electrolytic conduction in melt:

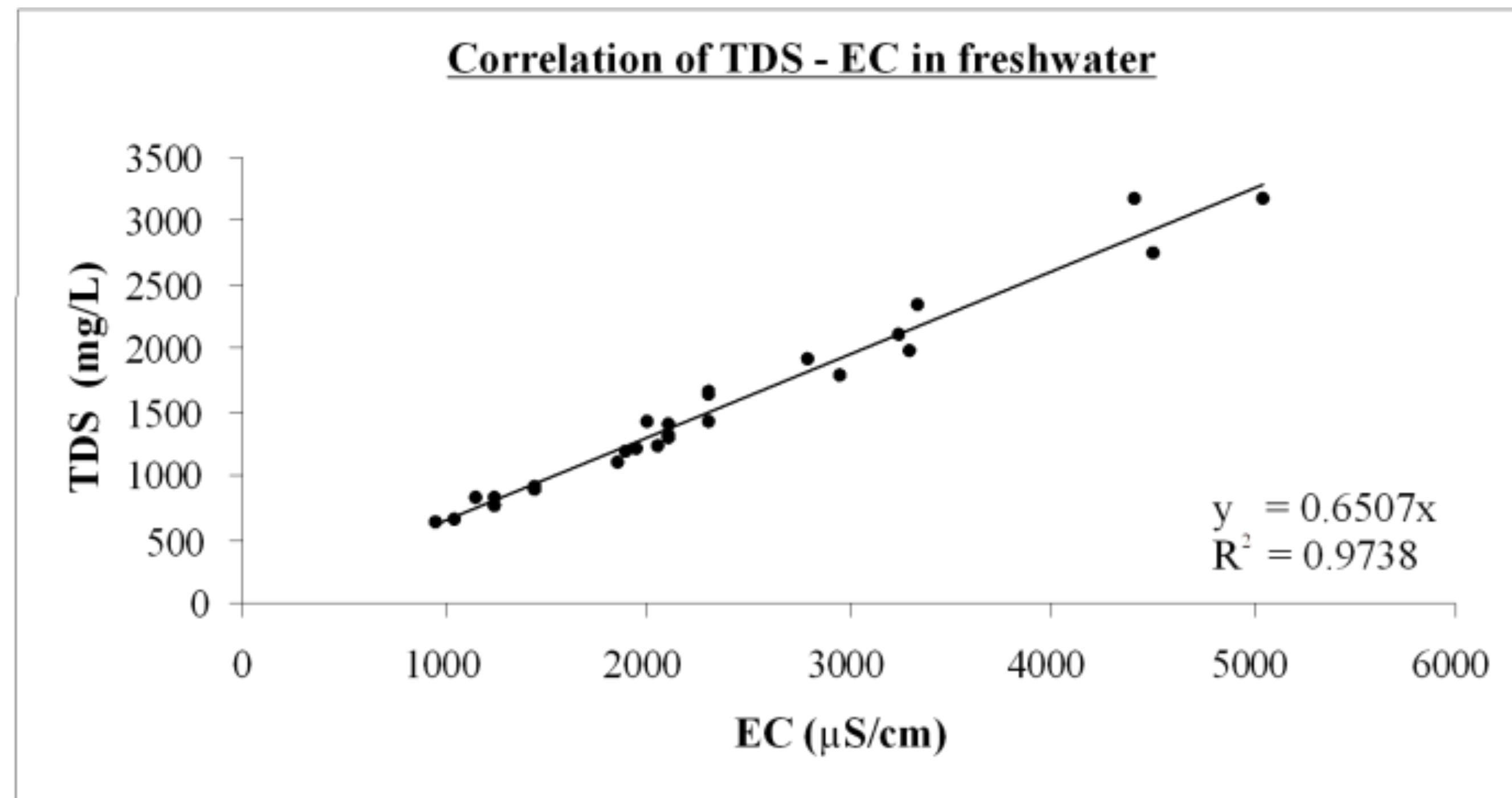
Olivine at 1000°C	0.0001 S/m	10,000 Ωm
Olivine at 1400°C	0.002 S/m	500 Ωm
Theoleite melt	3 S/m	0.3 Ωm
Silicate perovskite	1 S/m	1 Ωm

Ionic conduction:

Conductivity and total dissolved salts (TDS):

$$\sigma = a \times \text{TDS}$$

where TDS is in g/l and a is between 0.13 and 0.20, generally being lower for higher salinity.
For seawater $a = 0.143$. Temperature 20°C.



Ionic conduction:

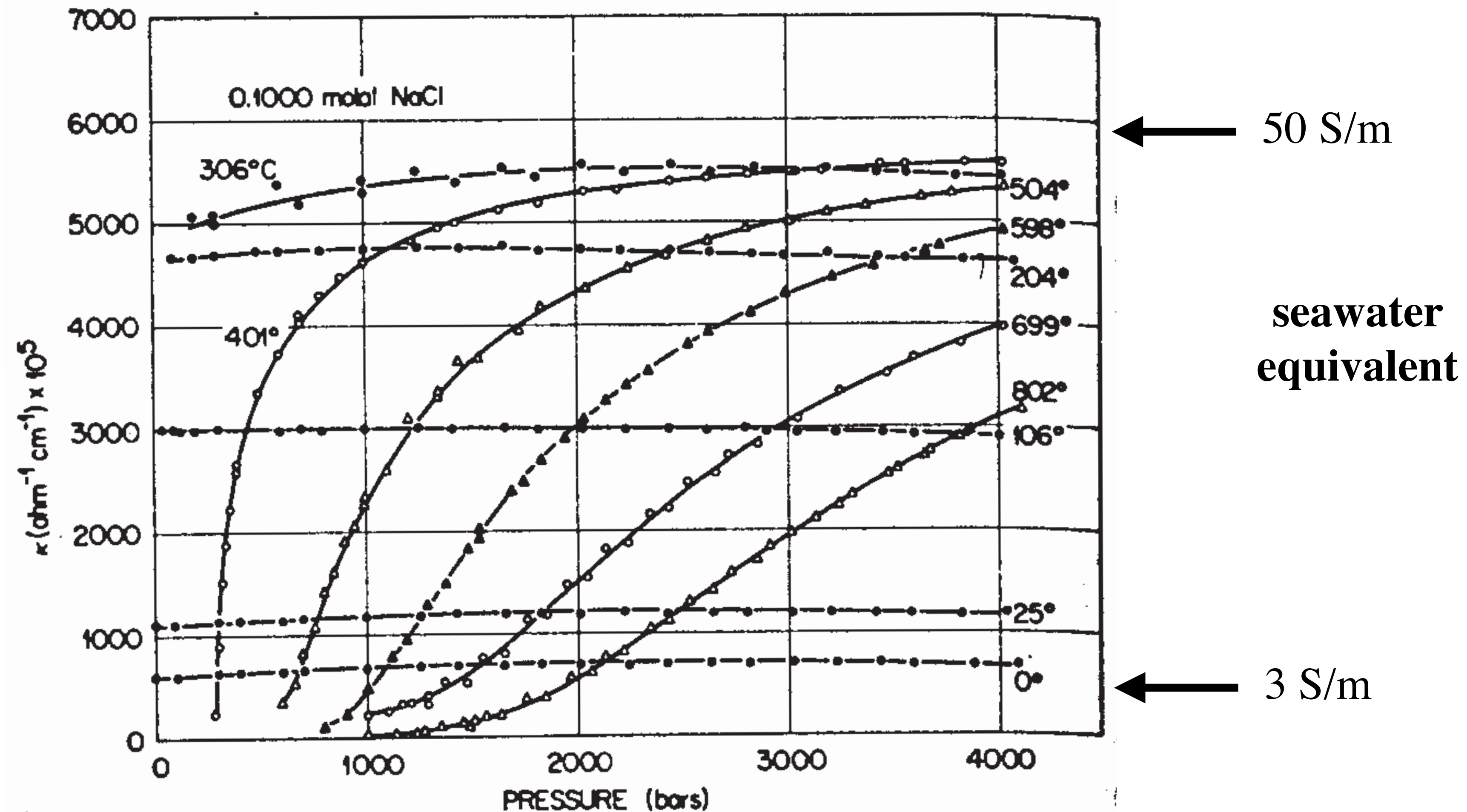
Electrical conductivity of seawater: $\sigma = 3 + T/10$ S/m

$$\sigma = 3 \text{ S/m} \quad T = 0^\circ\text{C}$$

$$\sigma = 5 \text{ S/m} \quad T = 20^\circ\text{C}$$

$$\sigma_f = 2.903916(1 + 0.0297175T + 0.00015551T^2 - 0.00000067T^3) \text{ S/m.}$$

High P & T:



Binary mixing laws:

There are various ways to model porosity and water/melt content. The most popular and venerable is Archie's Law:

$$\sigma = \sigma_s + (\sigma_f - \sigma_s)\beta^m$$

where the exponent m is between 1.5 and 2.0 (determined empirically) and

σ_s = conductivity of the mineral grains

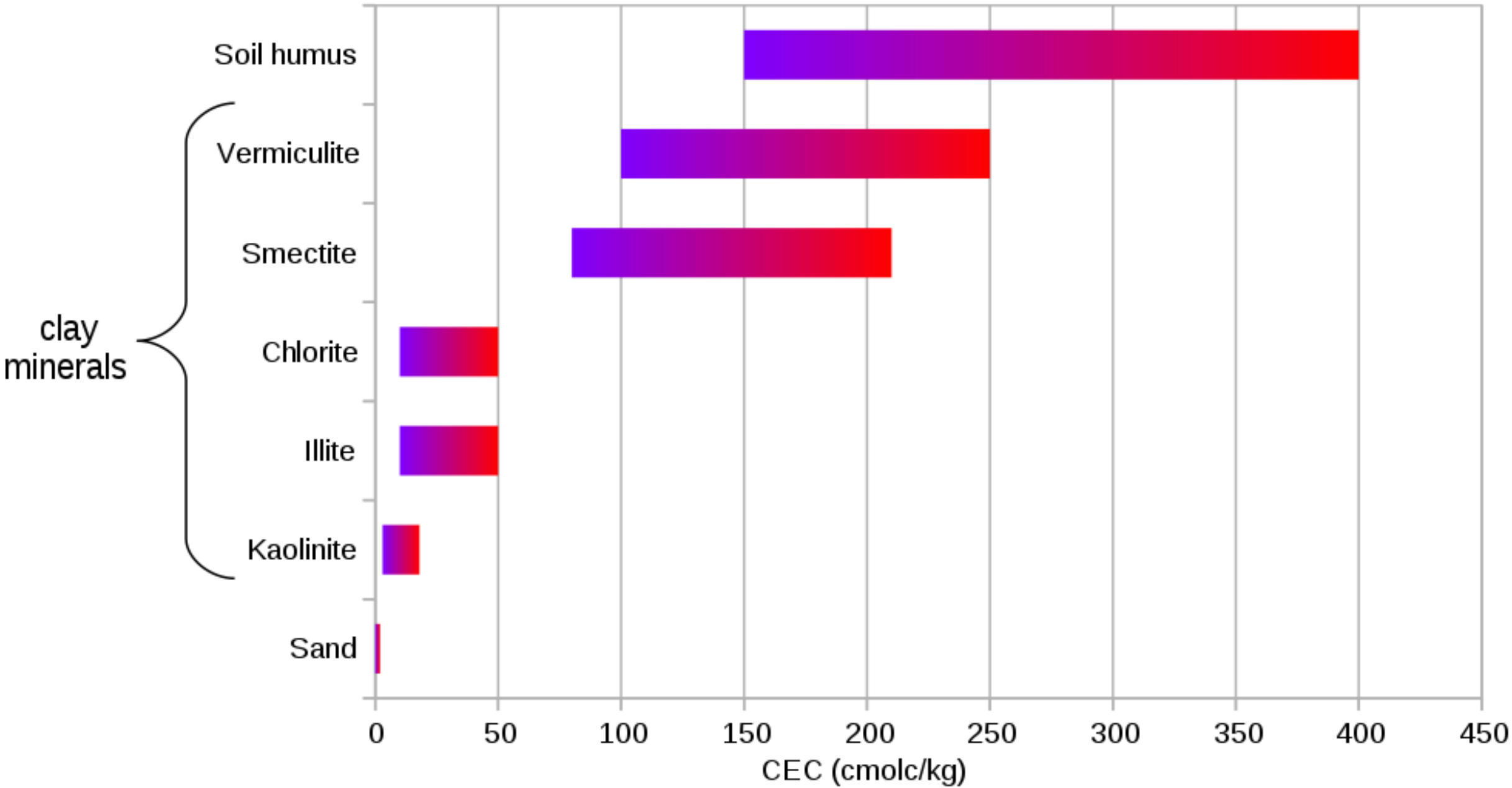
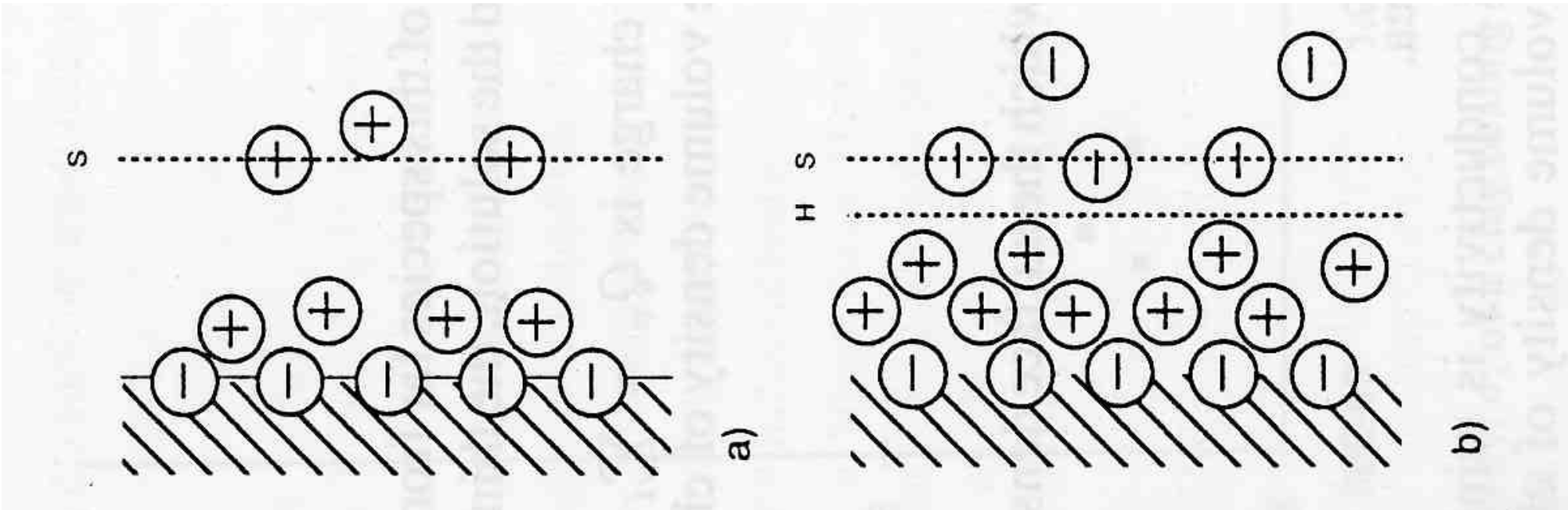
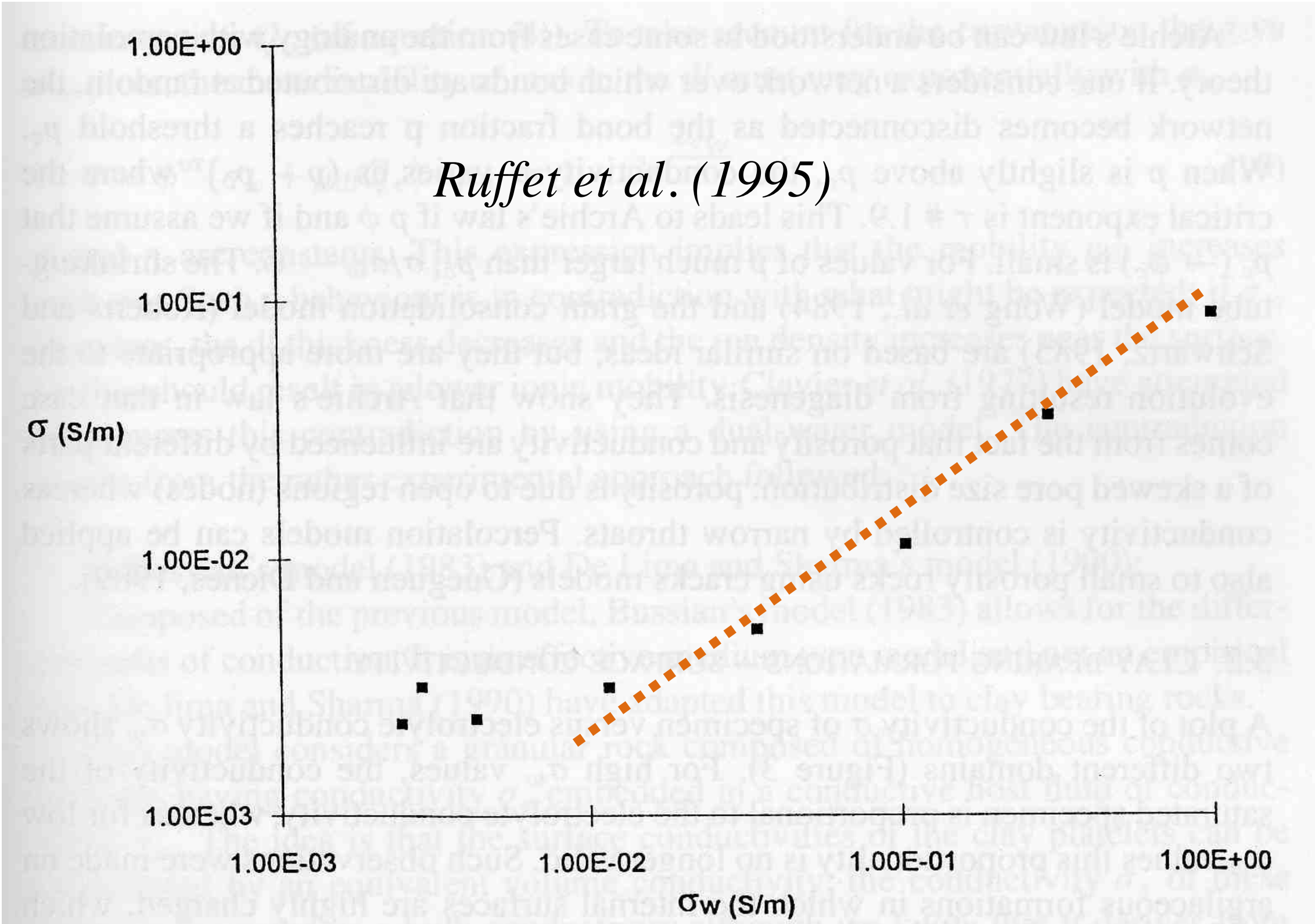
σ_f = conductivity of the fluid

β = fluid fraction (or porosity if saturated).

There are other models on which mixing laws can be based, for example fluid filled tubes:

$$\sigma = \frac{1}{3}\beta\sigma_f + (1 - \beta)\sigma_s$$

Clay-bearing sandstone (silty sandstone): For low pore water salinities, the layer of absorbed charge on the surface of clay minerals increases the conductivity. The density of this layer is measured by the *cation exchange capacity*.



Waxman-Smits (1968): $\sigma = \frac{1}{F^*}(BQ_V + \sigma_w)$

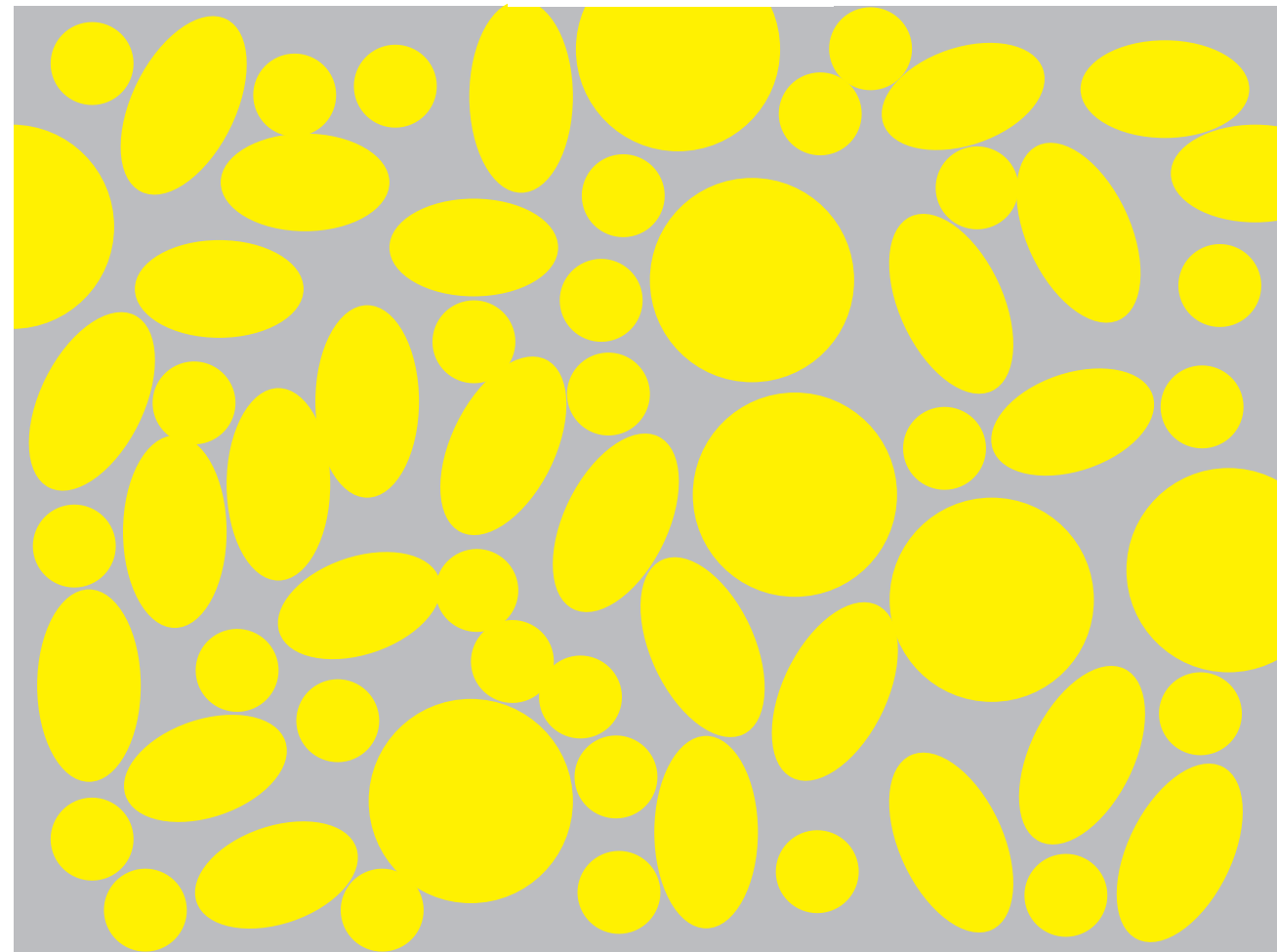
$$B = [1 - ae^{-\sigma_w/\gamma}]\lambda_{Na}^e \quad a = 1 - \frac{(\lambda_{Na}^e)_{\sigma_w=0}}{\lambda_{Na}^e}$$

All possible isotropic models must lie between the Hashin-Shtrikman (HS) bounds:

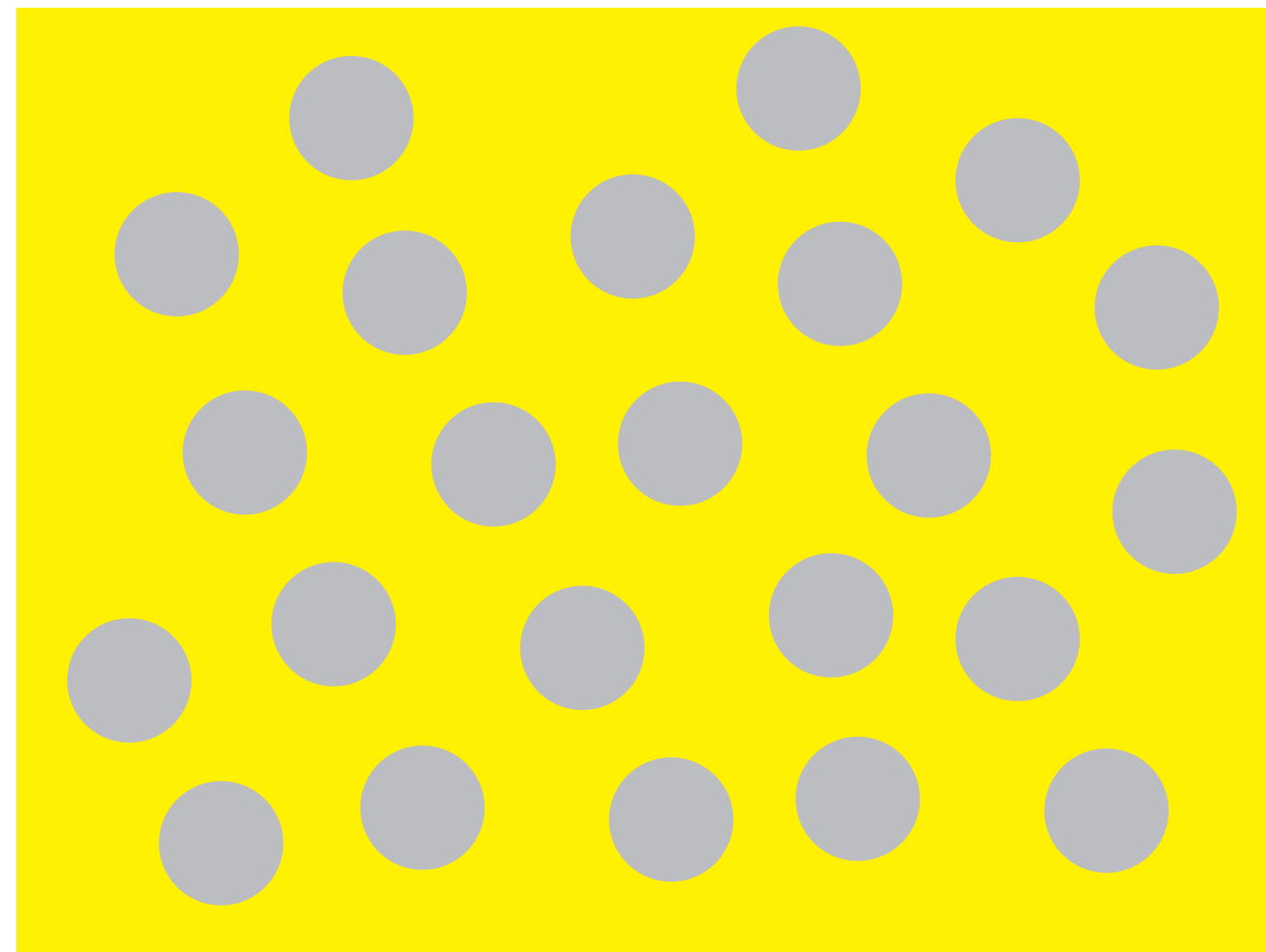
$$HS^- = \sigma_s + \beta \left(\frac{1}{\sigma_f - \sigma_s} + \frac{1 - \beta}{3\sigma_s} \right)^{-1}$$

$$HS^+ = \sigma_f + (1 - \beta) \left(\frac{1}{\sigma_s - \sigma_f} + \frac{\beta}{3\sigma_f} \right)^{-1}$$

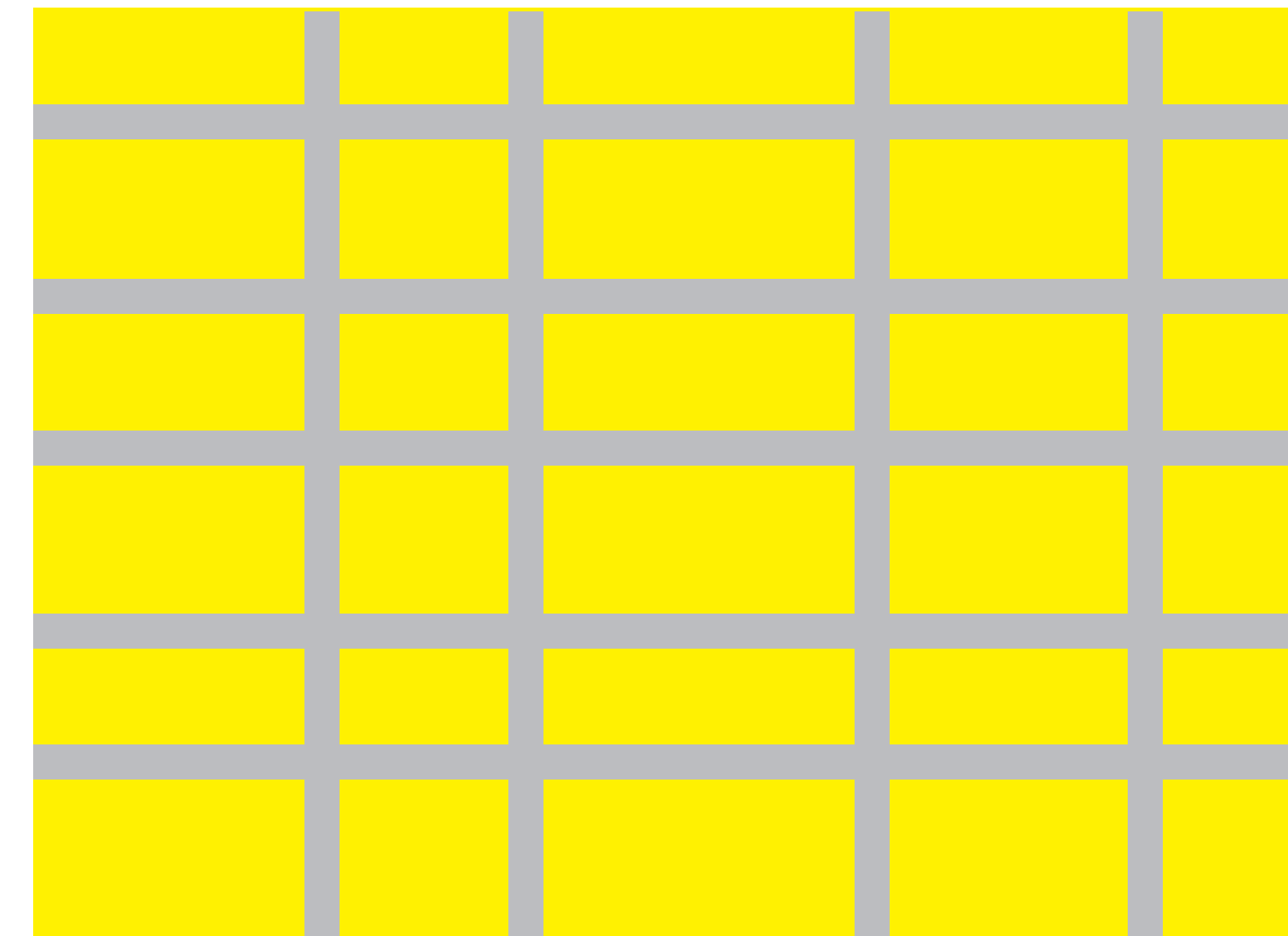
Archie's



HS - lower

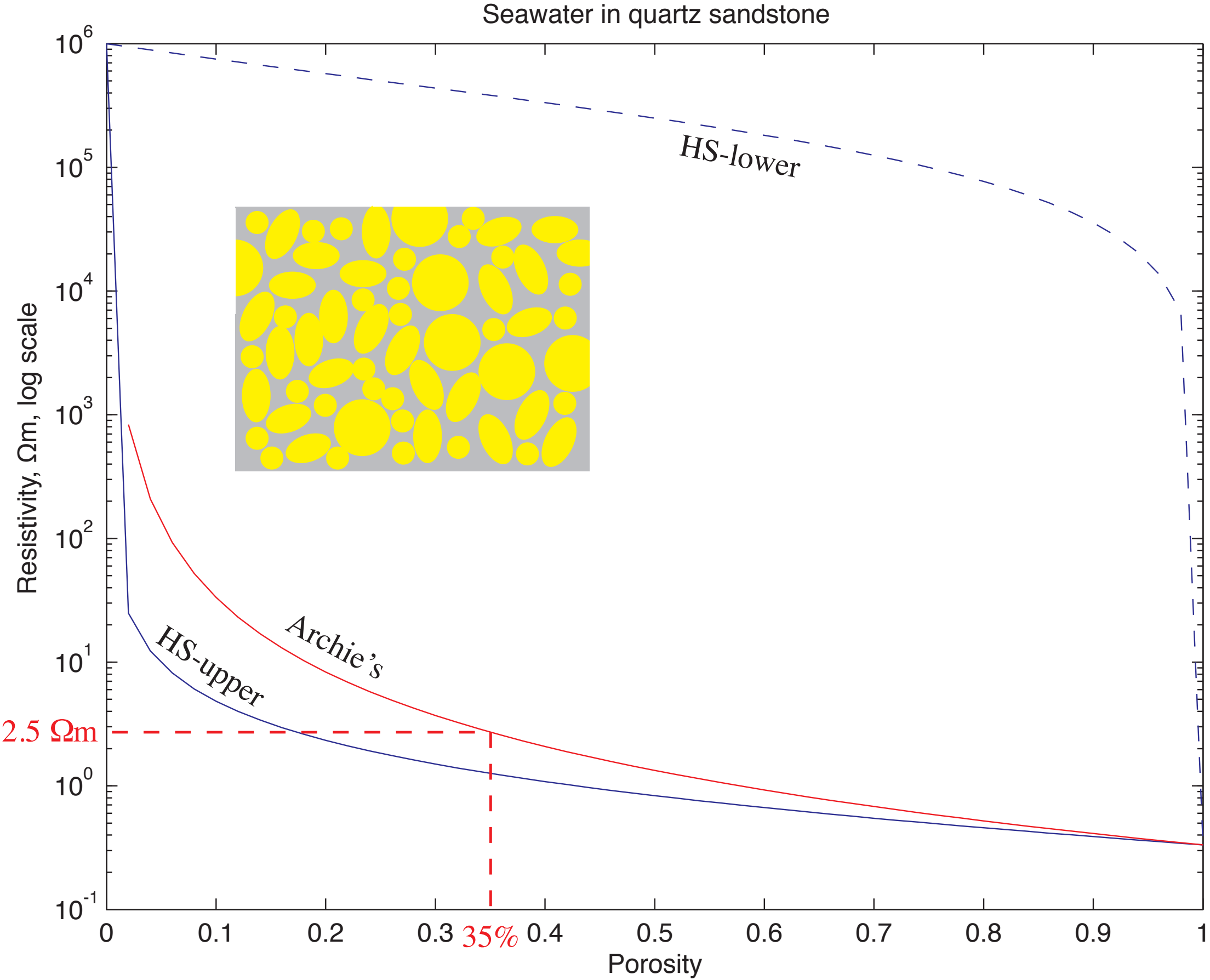


HS - upper

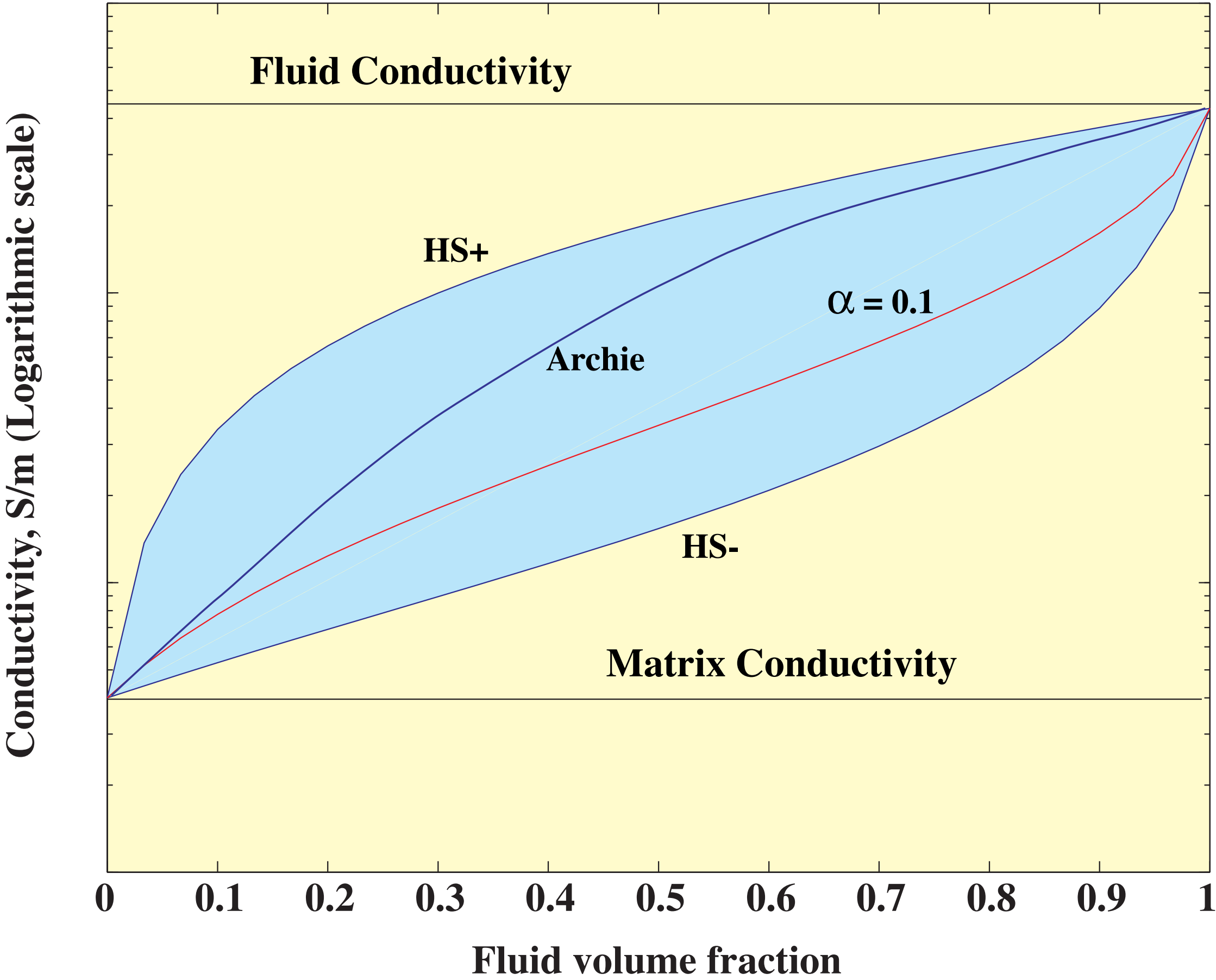


grey = conductor (melt, water) yellow = resistor (sand grains, sub-solidus mineral grains)

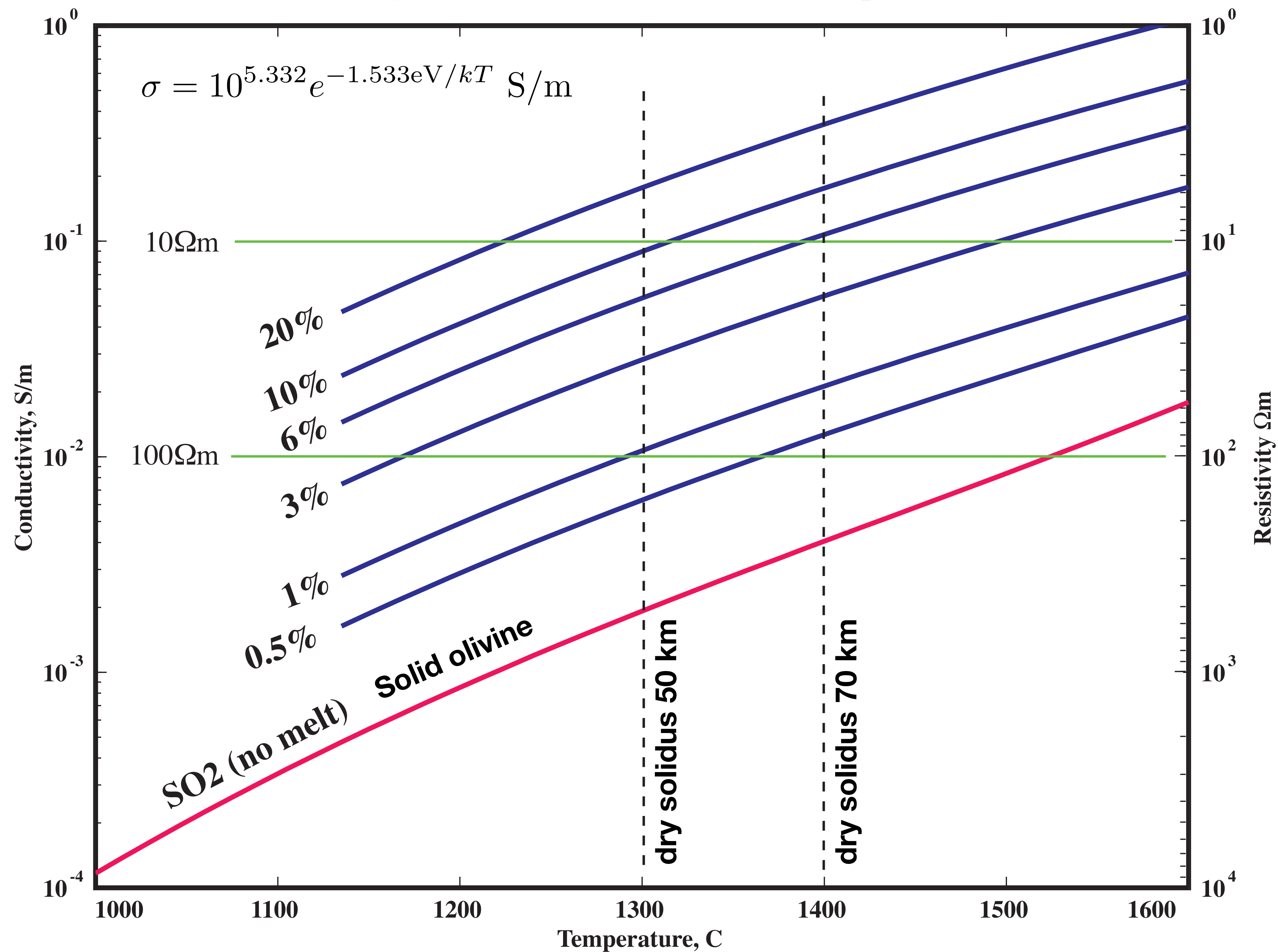
Seawater in sandstone:



Melt and hot minerals:



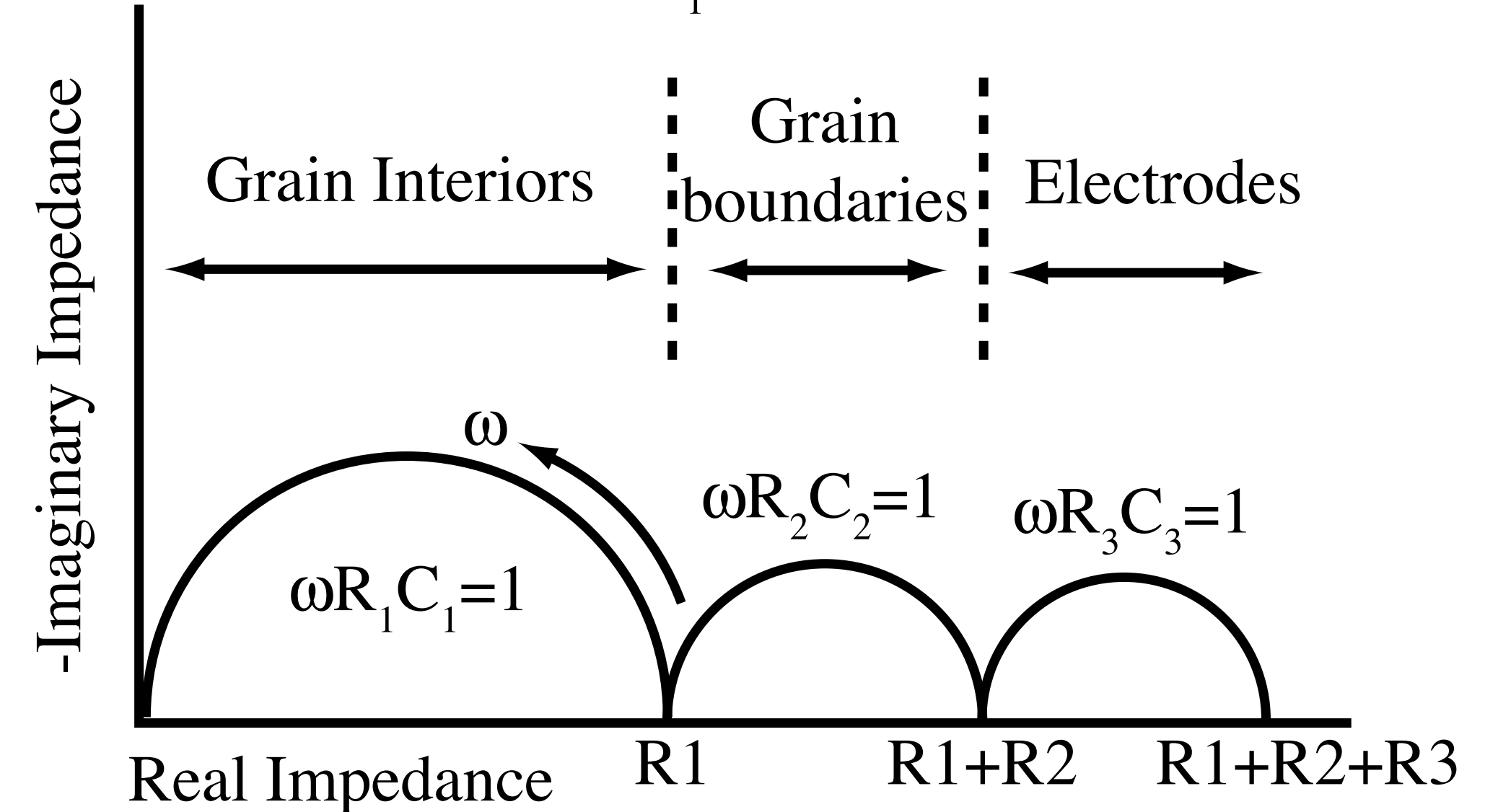
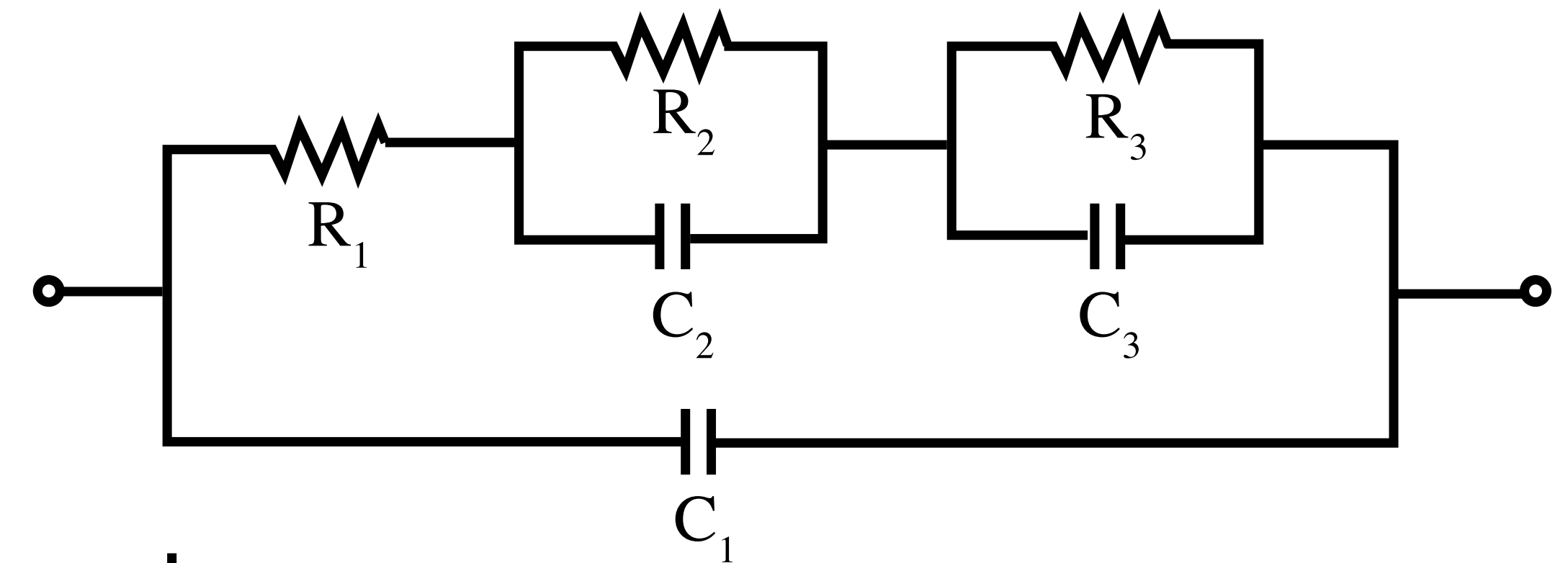
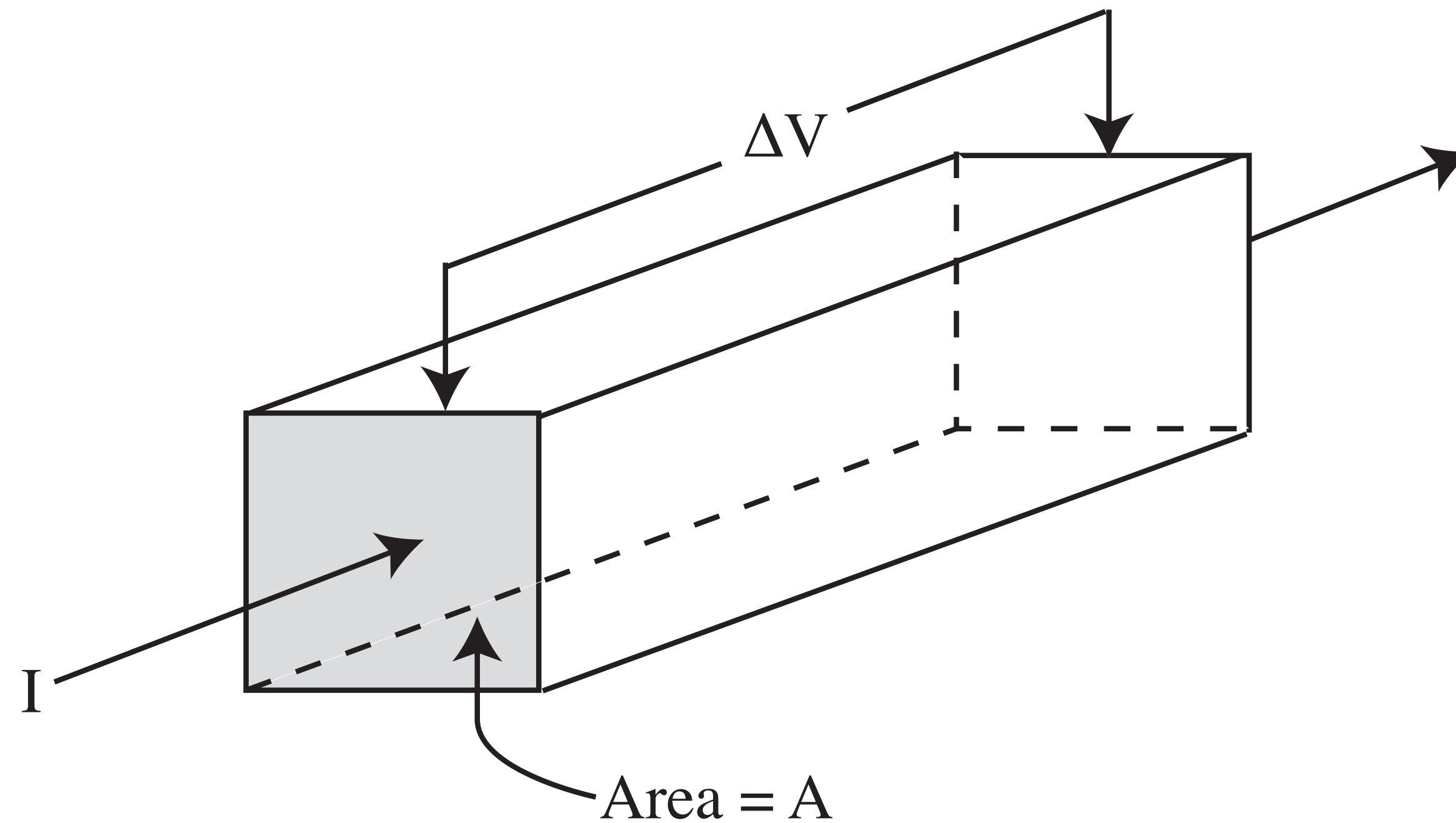
Conductivity Versus Melt Fraction and Temperature



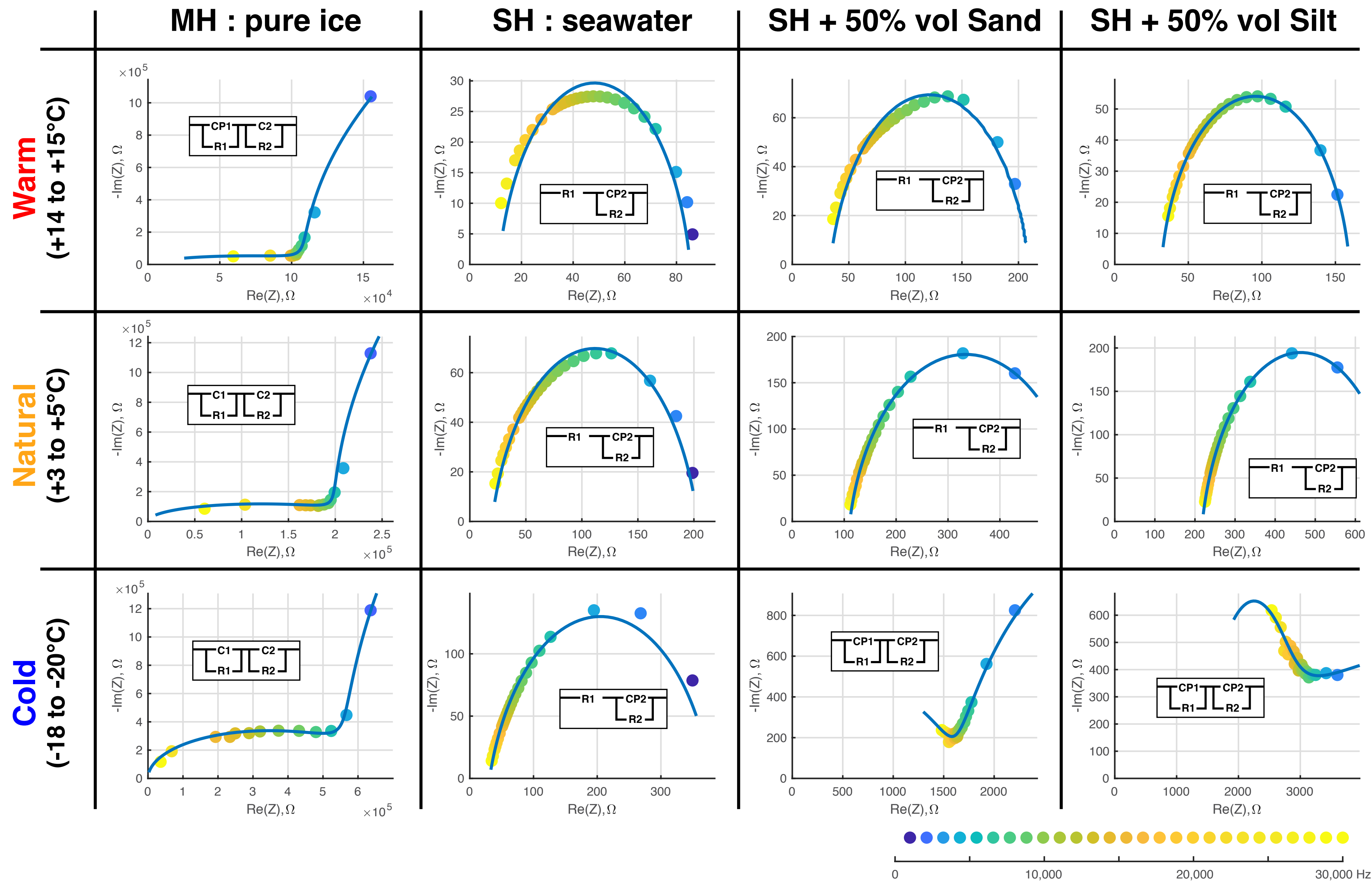
Measuring conductivity is simple in principle, but impedance spectroscopy is used to separate electrode polarization from sample conductivity, and even grain boundary effects in a multi-grain sample.

$$R = \Delta V / I$$

$$R = \rho L / A$$



Examples from methane hydrate + seawater + sand/silt:



Conductivity in metals

Moving an electric charge: $\sigma = nq\mu$

q is charge, n is concentration, μ is mobility, or drift velocity v per electric field $\left| \frac{v}{E} \right|$

Drift velocity of electrons in metals is $v = -eE\tau/m$

where $\mathcal{T}$ is the mean free time, m is mass. So, conductivity is $\sigma = \frac{ne^2\tau}{m}$

This can be thought of as an acceleration in an electric field (e/m) of charge density (ne) for a time $\mathcal{T}$. Drift velocity can be thought of as current density divided by charge density:

$$v = \frac{J}{c}$$

Typical values:

$$n \approx 10^{28} - 10^{29} \text{ /m}^3 \quad v \approx 10^{-4} \text{ m/s} \quad \sigma \approx 10^7 \text{ S/m}$$

$$v\tau \approx 10^{-2} \text{ m at } 4 \text{ K} \quad v\tau \approx 10^{-8} \text{ m at } 20^\circ \text{C}$$

Semiconduction:

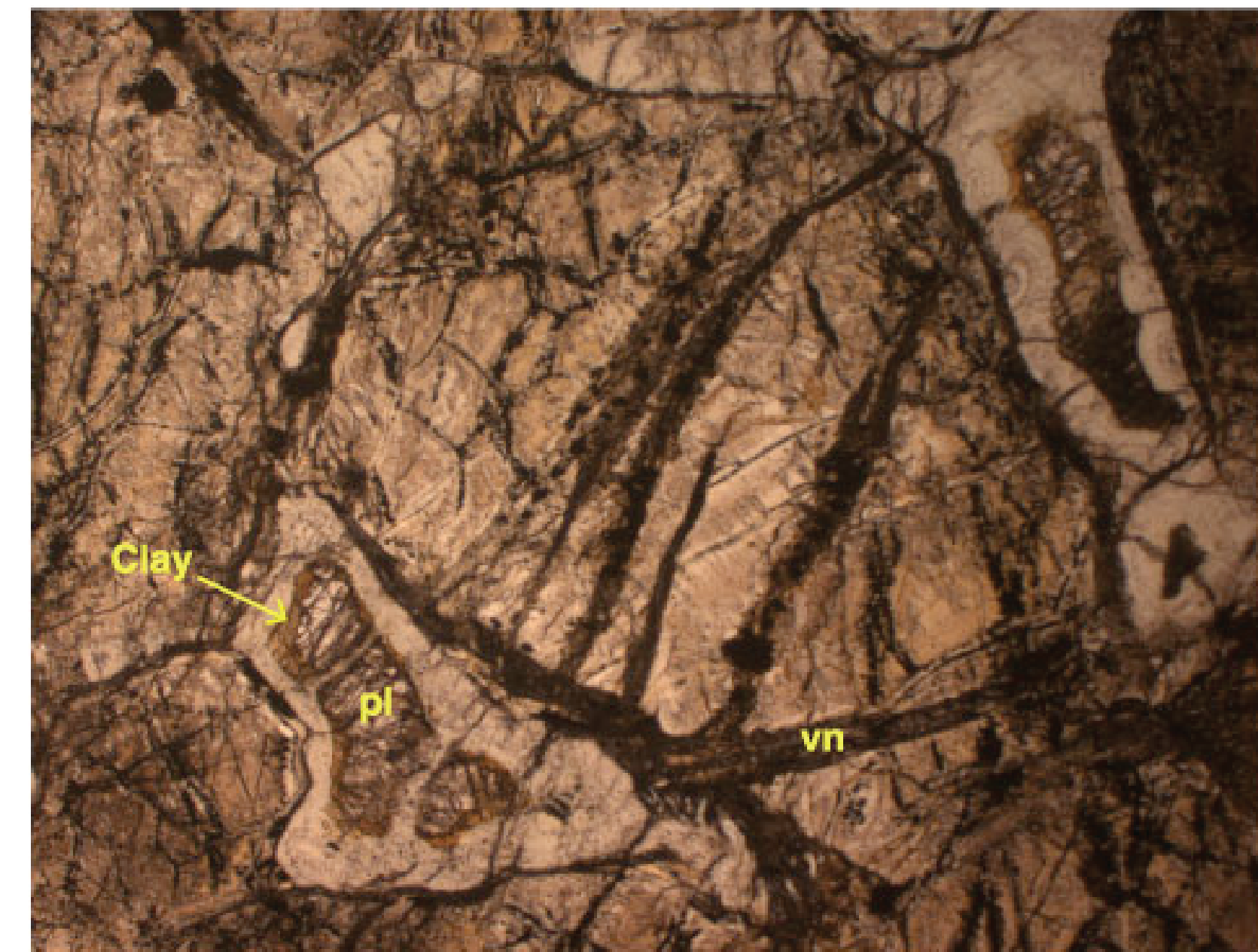
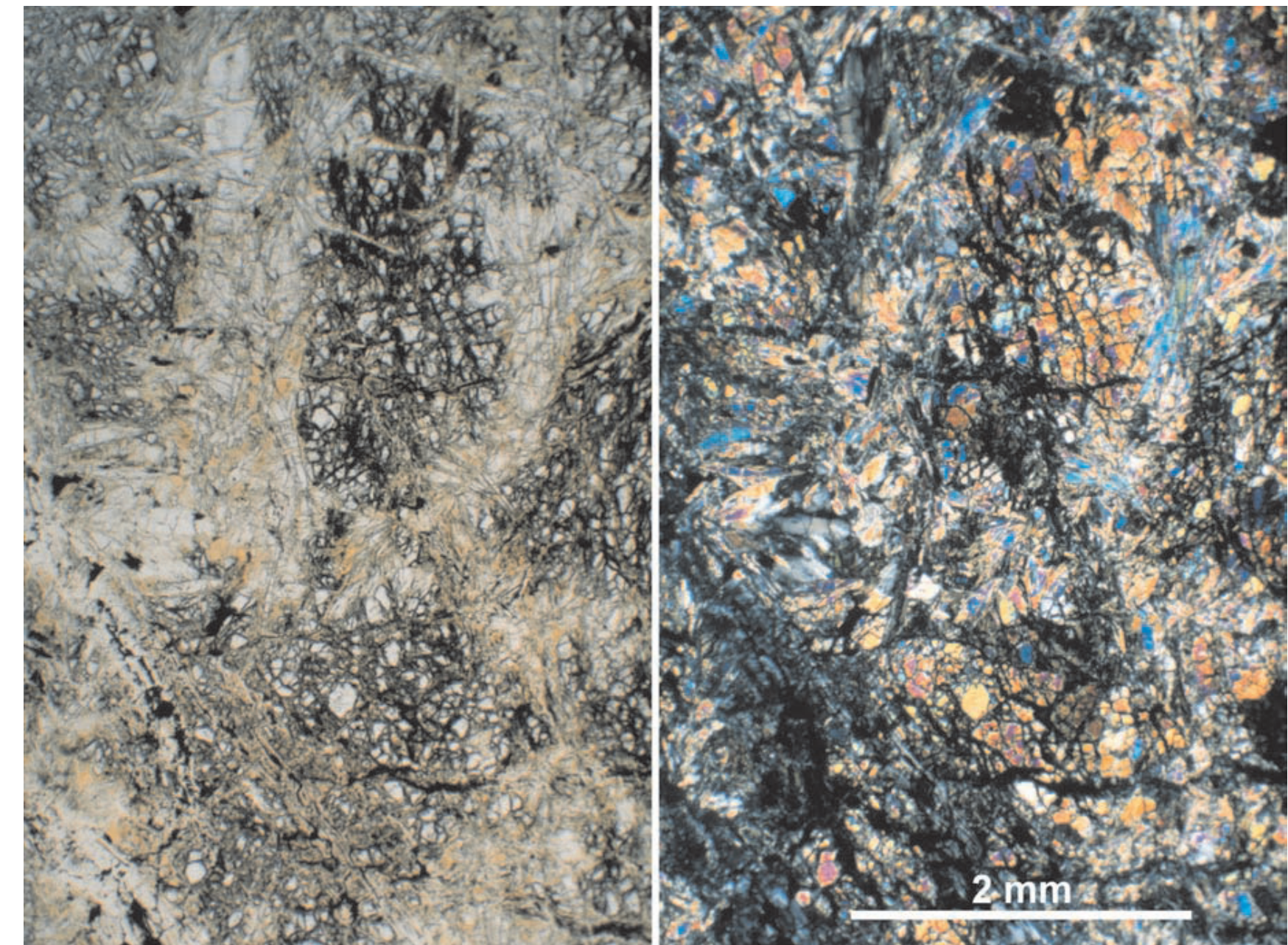
Ore minerals are generally semiconductors.

Other conductive mineral phases can form a connected path through rocks. Serpentinization can create halos of connected magnetite around relic olivine grains.

It has been suggested that cumulate magnetite in layered intrusions is responsible for lower crustal conductors in rifted margins.

It has also been suggested that sulfides on grain boundaries of mantle minerals increases the conductivity beneath the Sierra Nevada.

Graphite precipitated from CO₂ fluids in the crust has also been implicated to explain high conductivity.



Serpentinite.

Mineral electrical conductivity as a function of pressure and temperature really is parameterized.

Each conduction mechanism is described by a thermally-activated Boltzmann process:

$$\sigma = \sum_i \sigma_i e^{-E_i/kT}$$

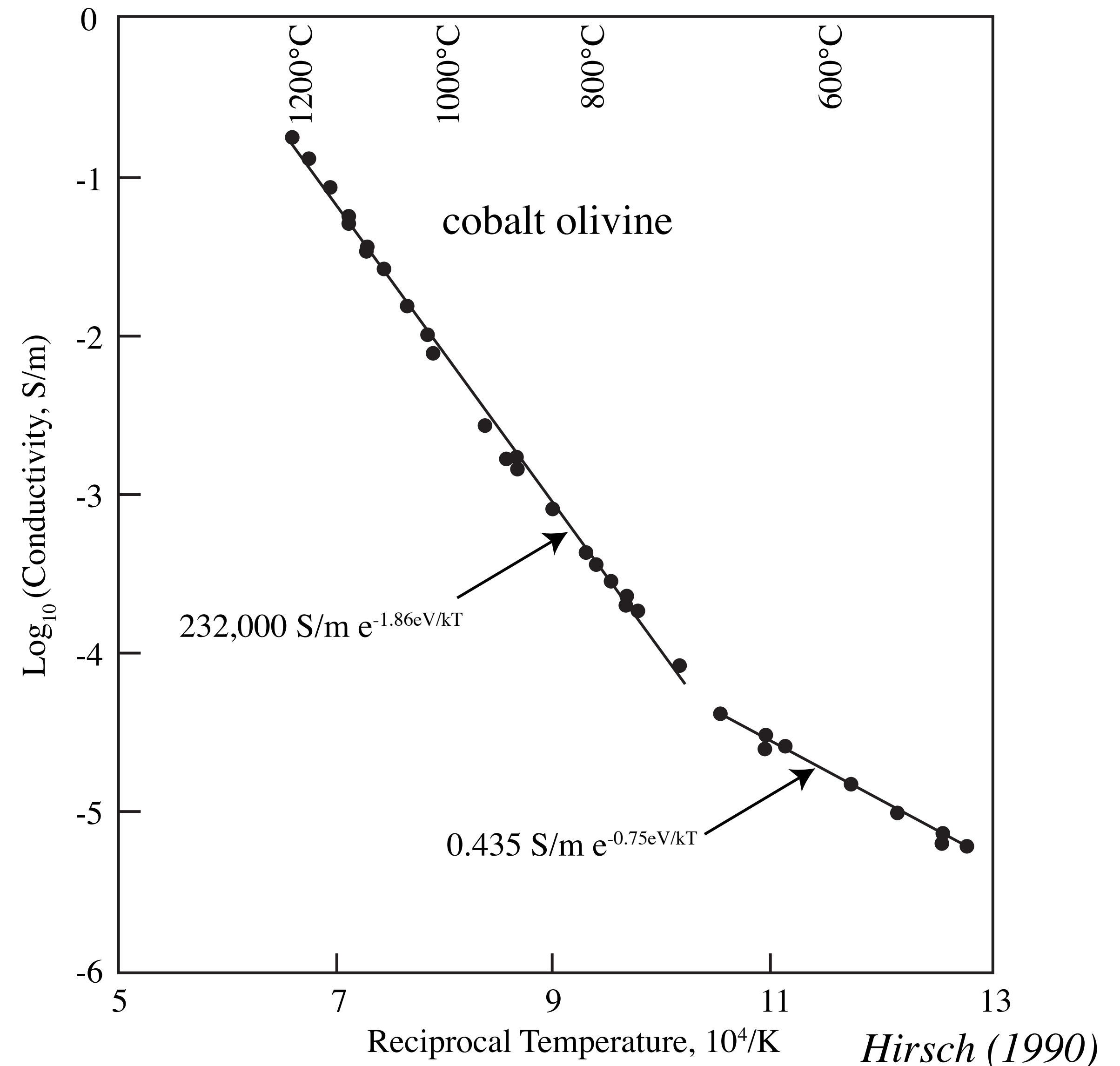
σ is conductivity, S/m

T is absolute temperature, Kelvin

E is activation energy

k is Boltzmann's constant

These are called Arrhenius relationships, and can be linearized by plotting $\log(\sigma)$ against $1/T$. The slope gives E_A



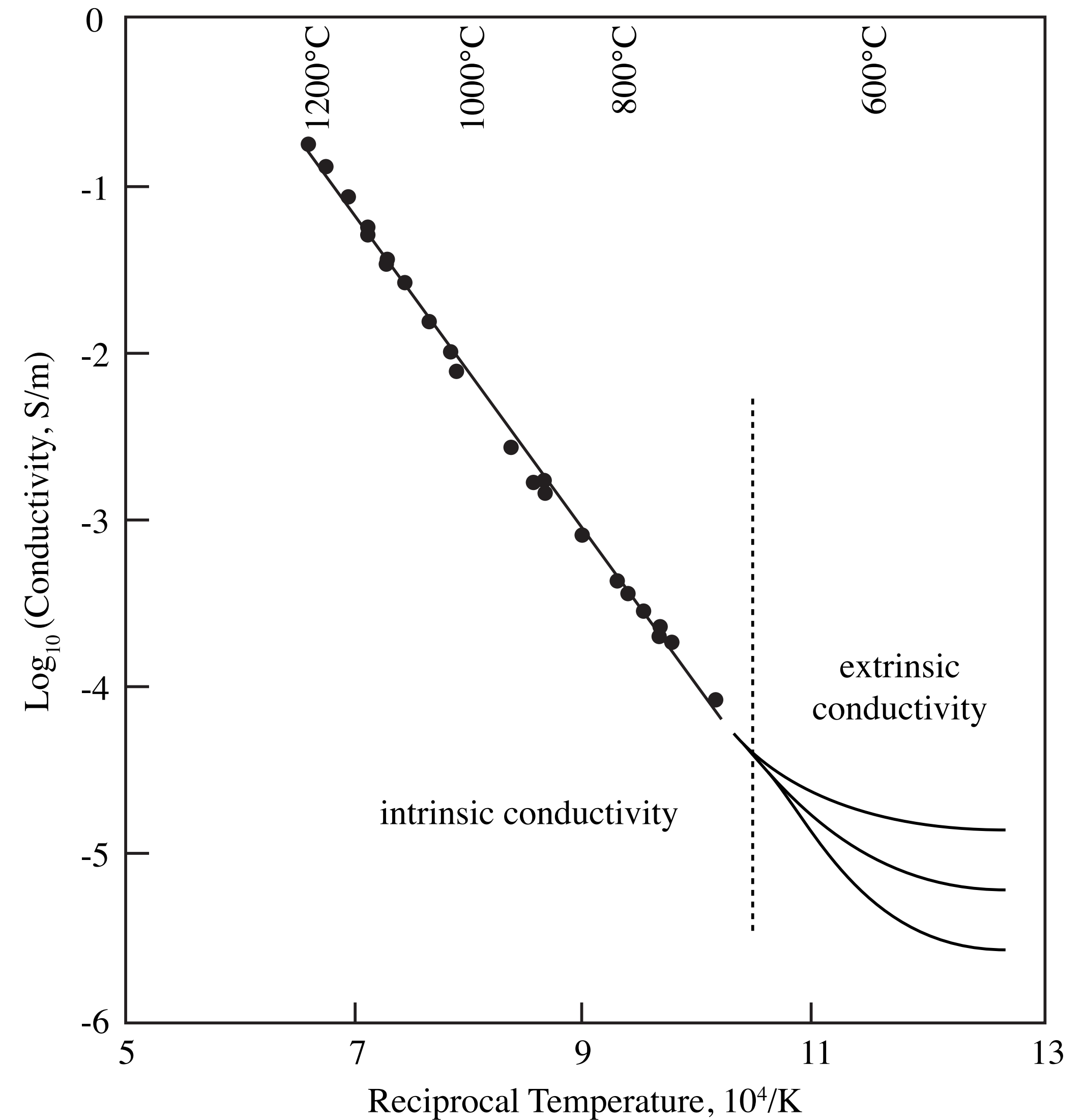
Semiconductors

$$\sigma = ne\mu_e + pe\mu_h$$

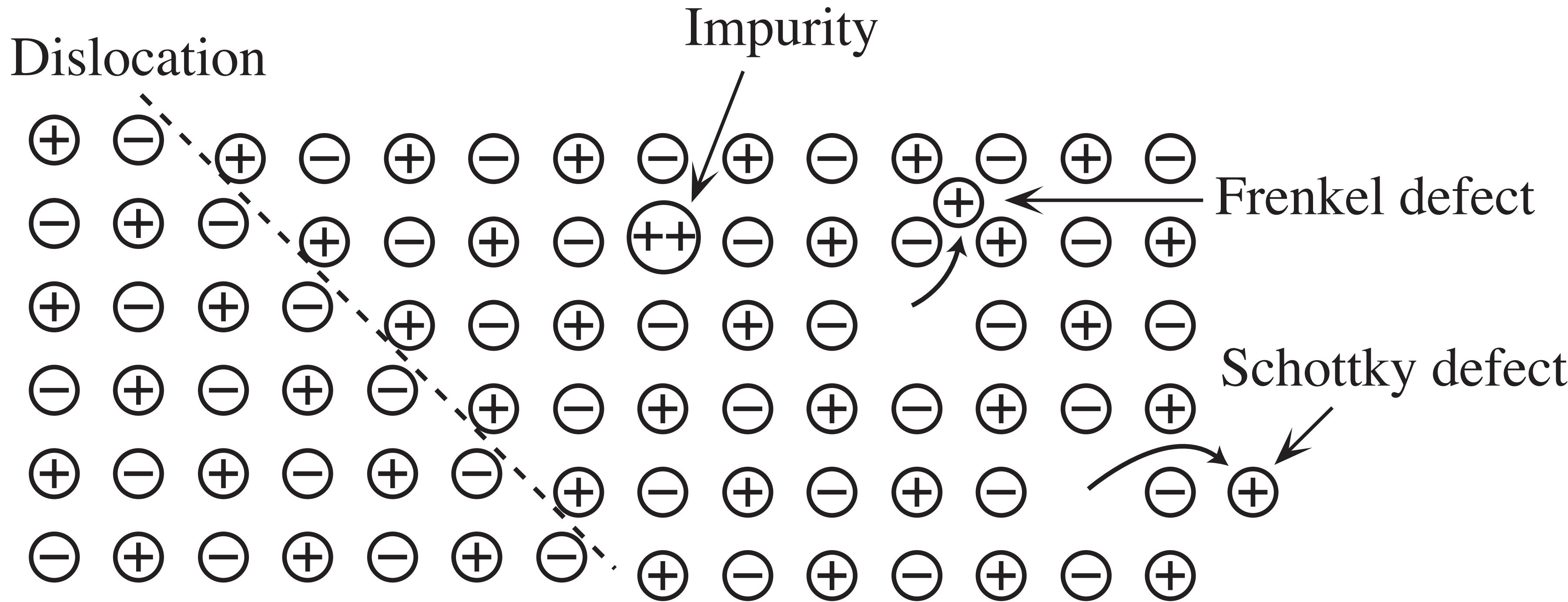
$$n \propto T^{3/2} e^{-E_g/2kT}$$

Intrinsic conduction is a result of thermally activated electrons and holes. All samples of a given material behave the same.

Extrinsic conduction is a result of impurities which donate either electrons or holes to conduction. The amount of impurity will vary from sample to sample.



Defect conduction:



$$n_s = N e^{-E_v/kT}$$

Schottky defects or vacancies

$$n_f = (N N')^{1/2} e^{-E_i/2kT}$$

Frenkel defects or interstitials

Fick's Law:

$$\mathbf{J}_N = -D\nabla N$$

$\mathbf{J}$ is the flux of a species and D is diffusivity or diffusion constant

$$D = D_o e^{-E_d/kT}$$

The Nernst-Einstein equation relates mobility μ to diffusivity

$$kT\mu = qD$$

Using $\sigma = nq\mu$ and substituting for the mobility and the concentration for Schottky defects we get

$$\sigma = Nq^2 D_o / kT e^{-E_v/kT} e^{-E_d/kT}$$

 **concentration**  **mobility**

But the exponentials dominate, and so to a good approximation

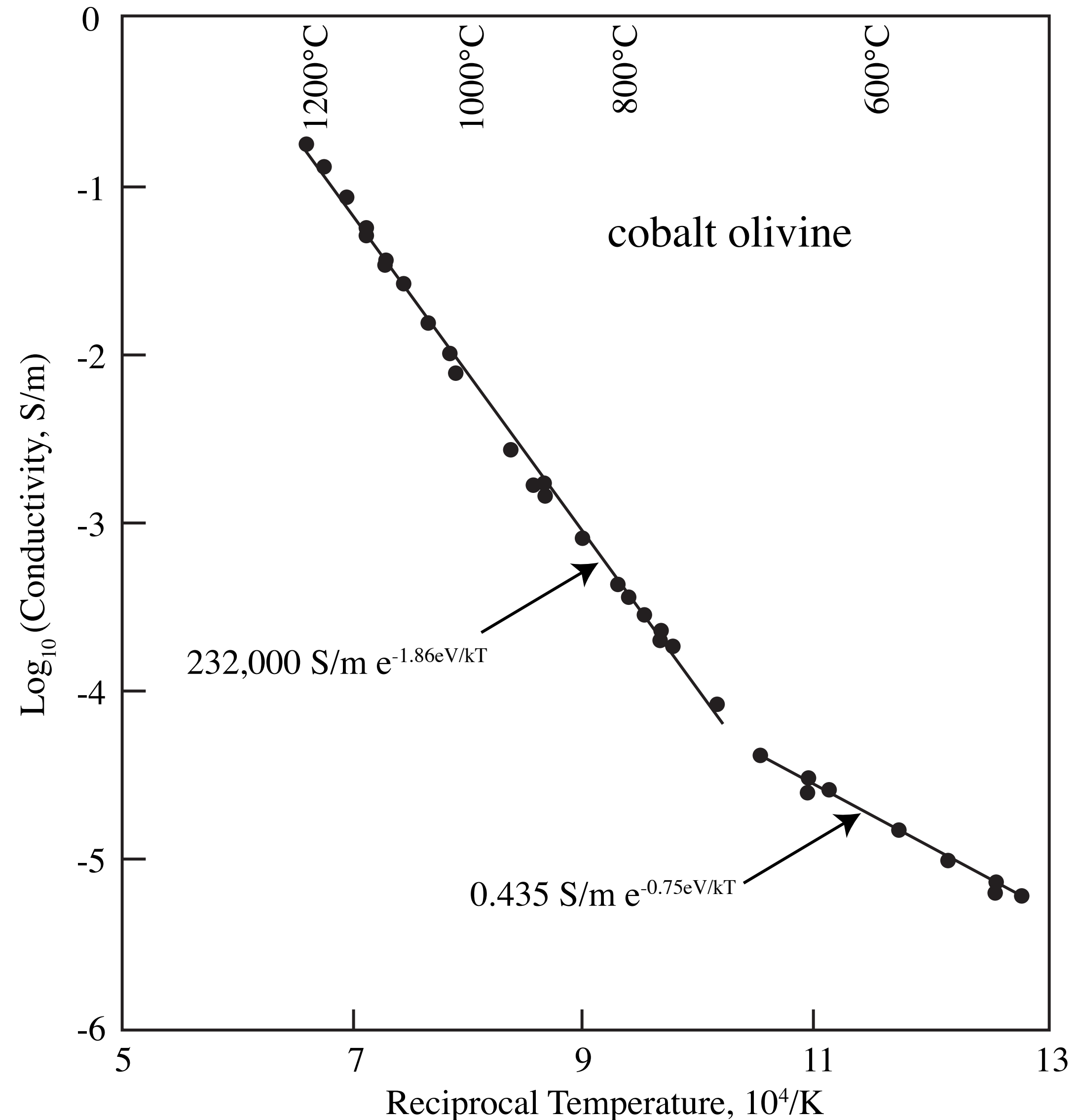
$$\sigma = \sigma_o e^{-E/kT}$$

If we have multiple conduction species then conductivity is just the sum. But exponentials dominate at particular temperatures.

$$\sigma = \sum_i \sigma_i e^{-E_i/kT}$$

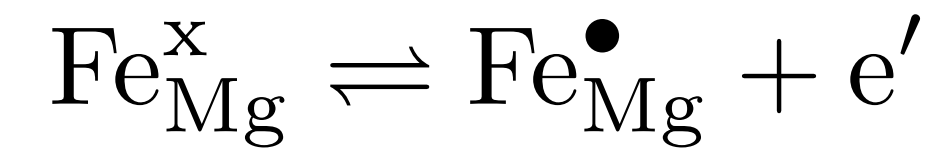
Sometimes one has to include a pressure effect:

$$\sigma = \sigma_o e^{-(E+P\Delta V)/kT}$$

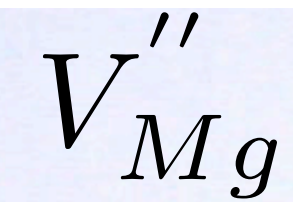
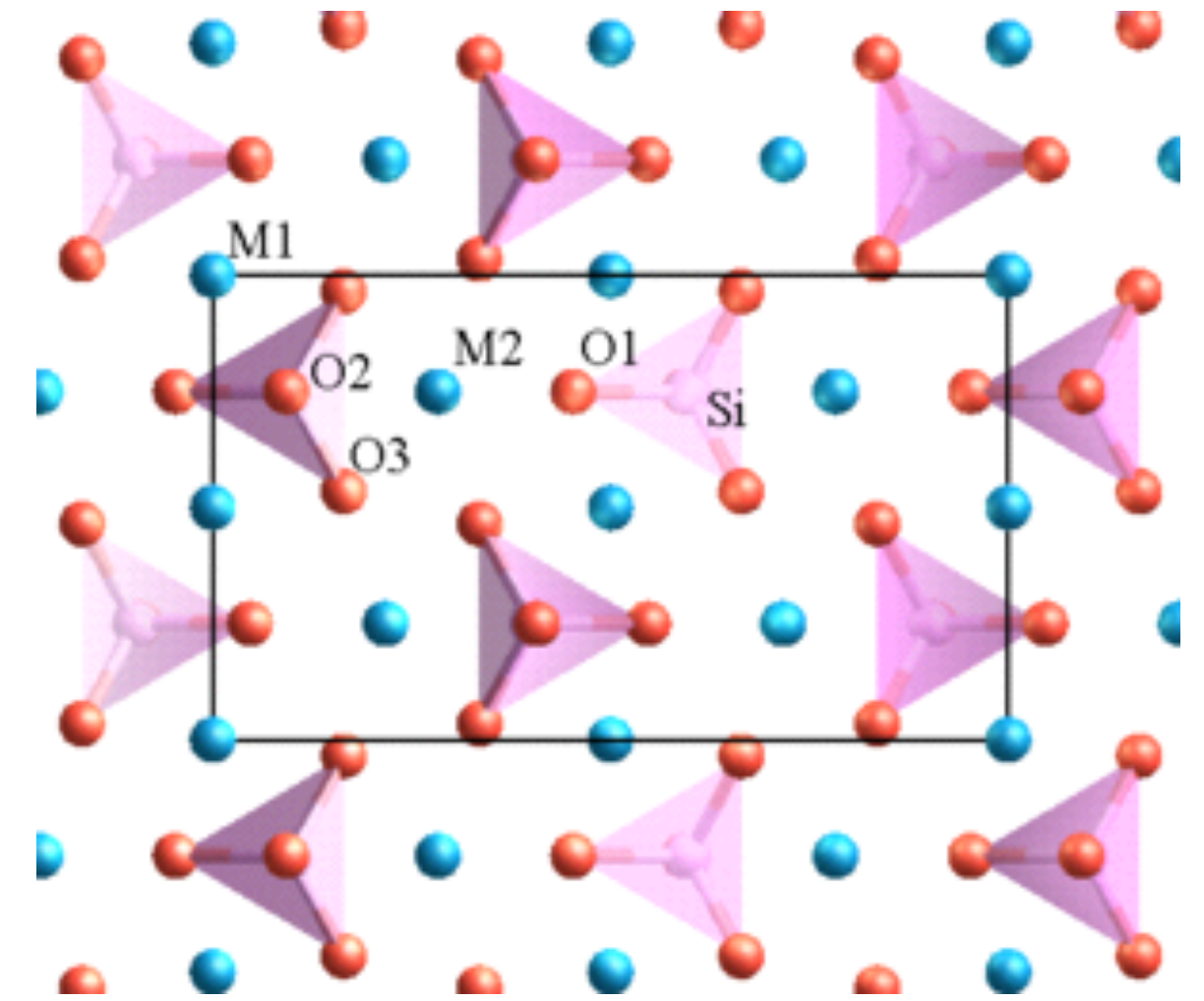
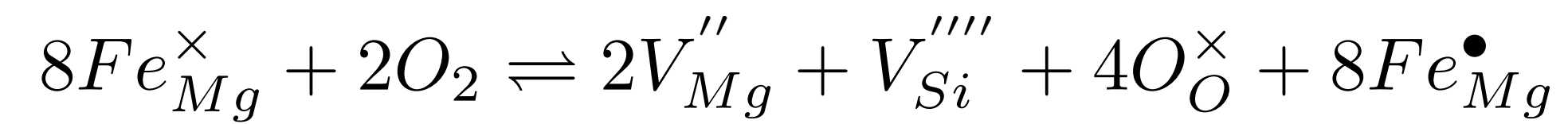


Hirsch (1990)

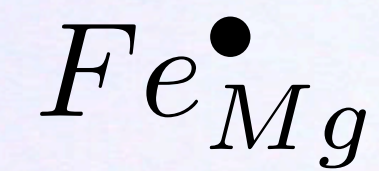
Oxidation of iron:



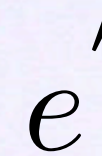
Oxidation of olivine ($Mg_{0.9}Fe_{0.1}SiO_4$):



magnesium vacancies



“small polaron”

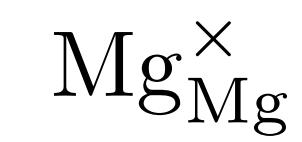
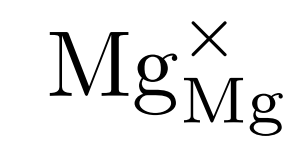
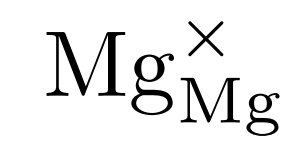
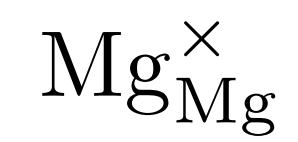
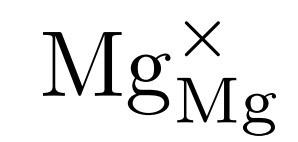
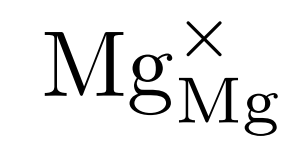
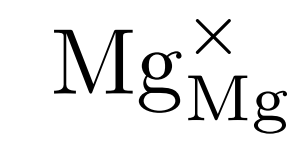
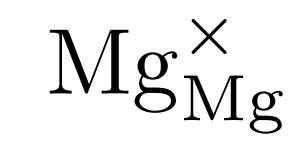
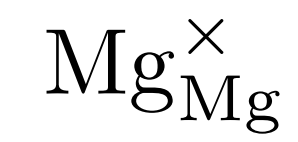
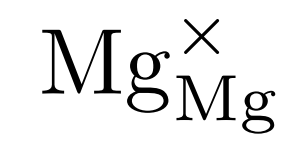
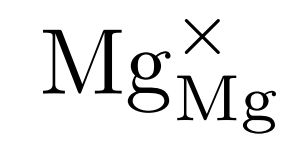
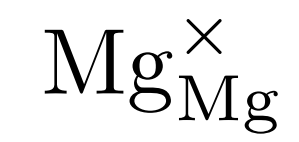
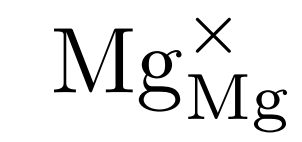
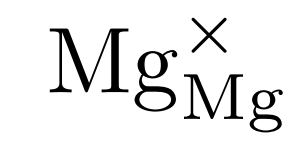
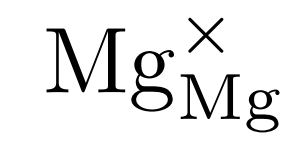
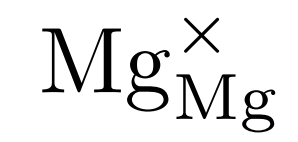
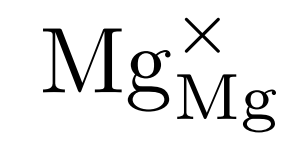
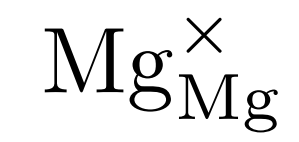
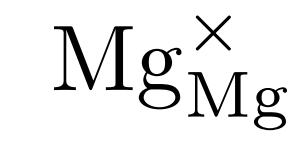
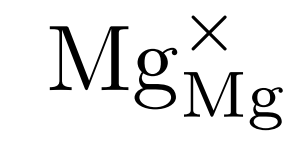
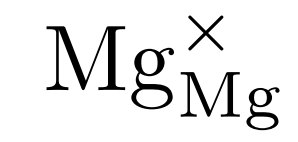
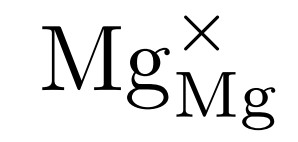
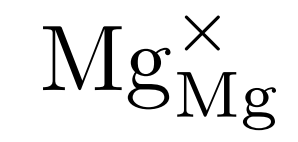
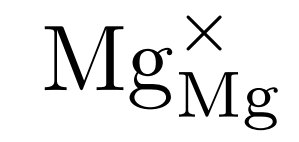


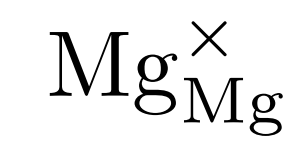
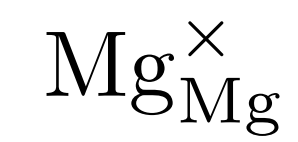
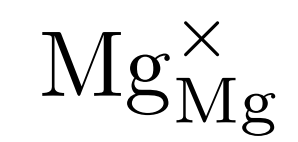
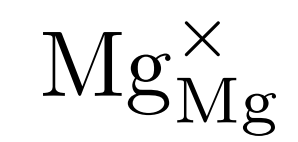
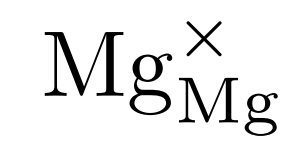
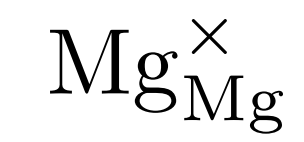
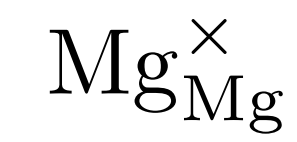
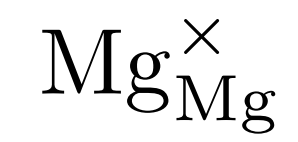
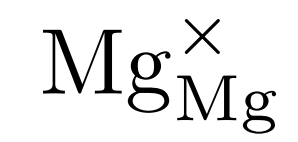
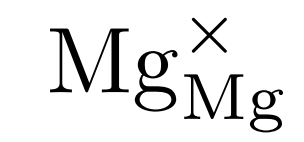
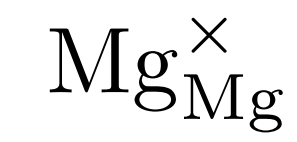
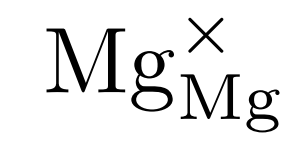
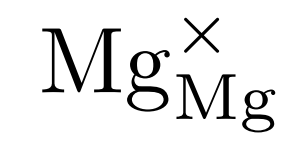
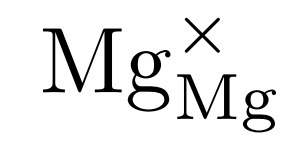
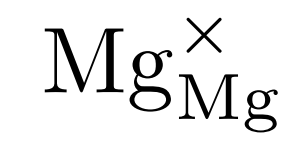
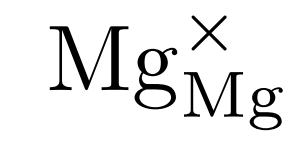
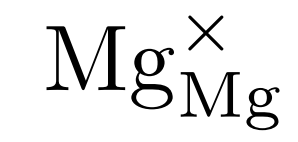
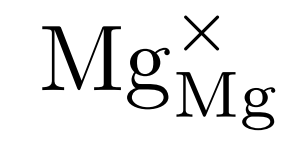
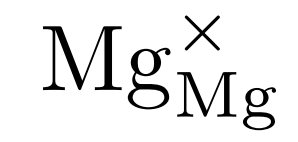
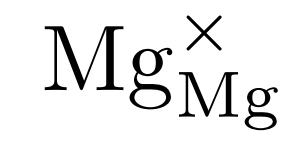
electron



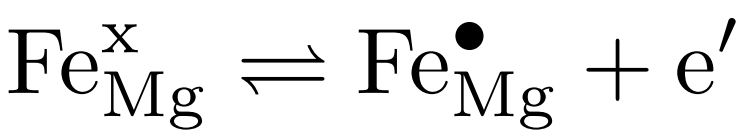
silicon vacancies

Forsterite Mg_2SiO_4



Olivine $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_4$ 

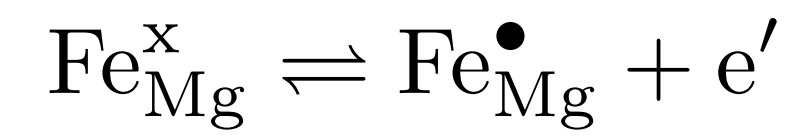
Oxidation of iron:



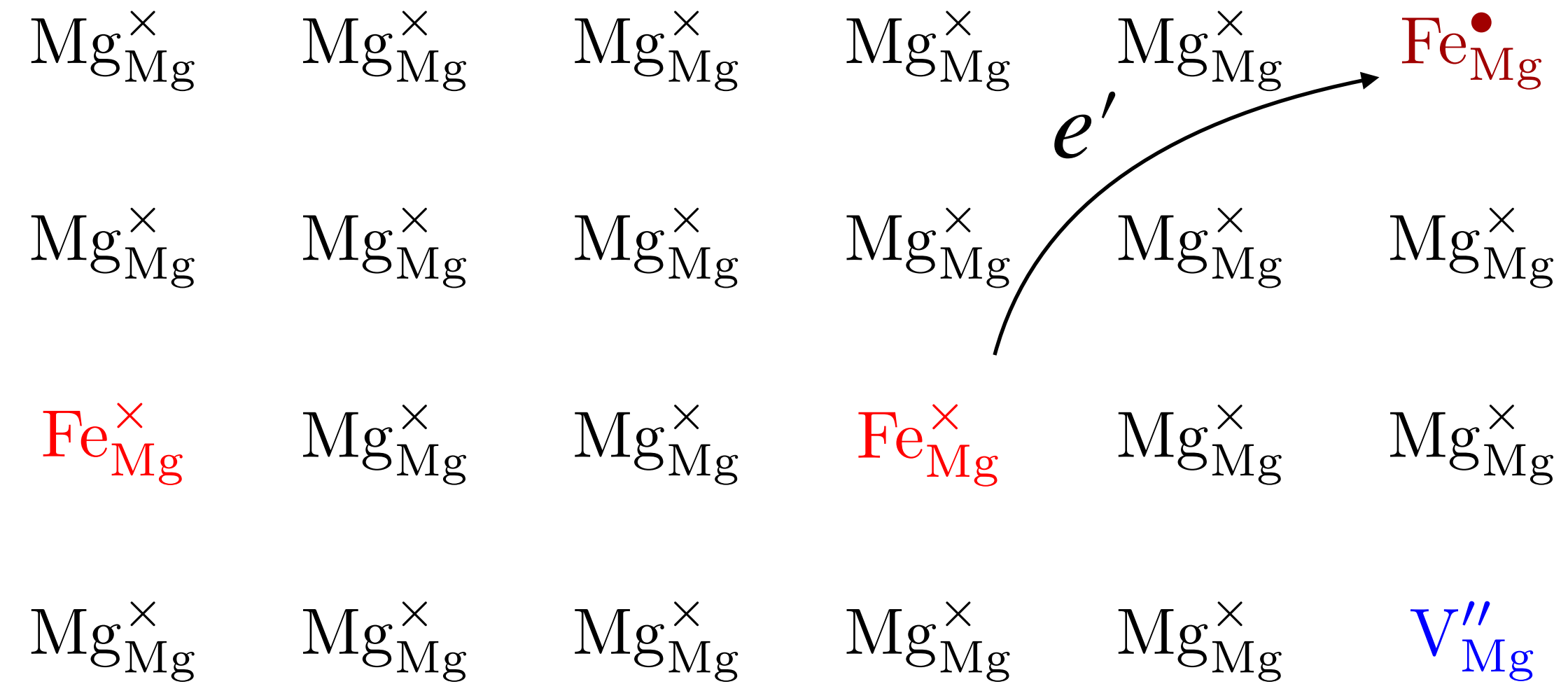
Olivine $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_4$ with defects



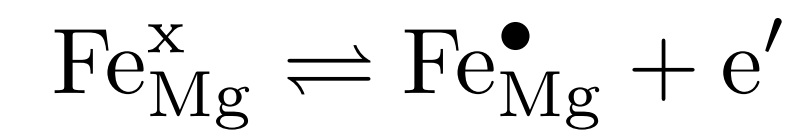
Oxidation of iron:



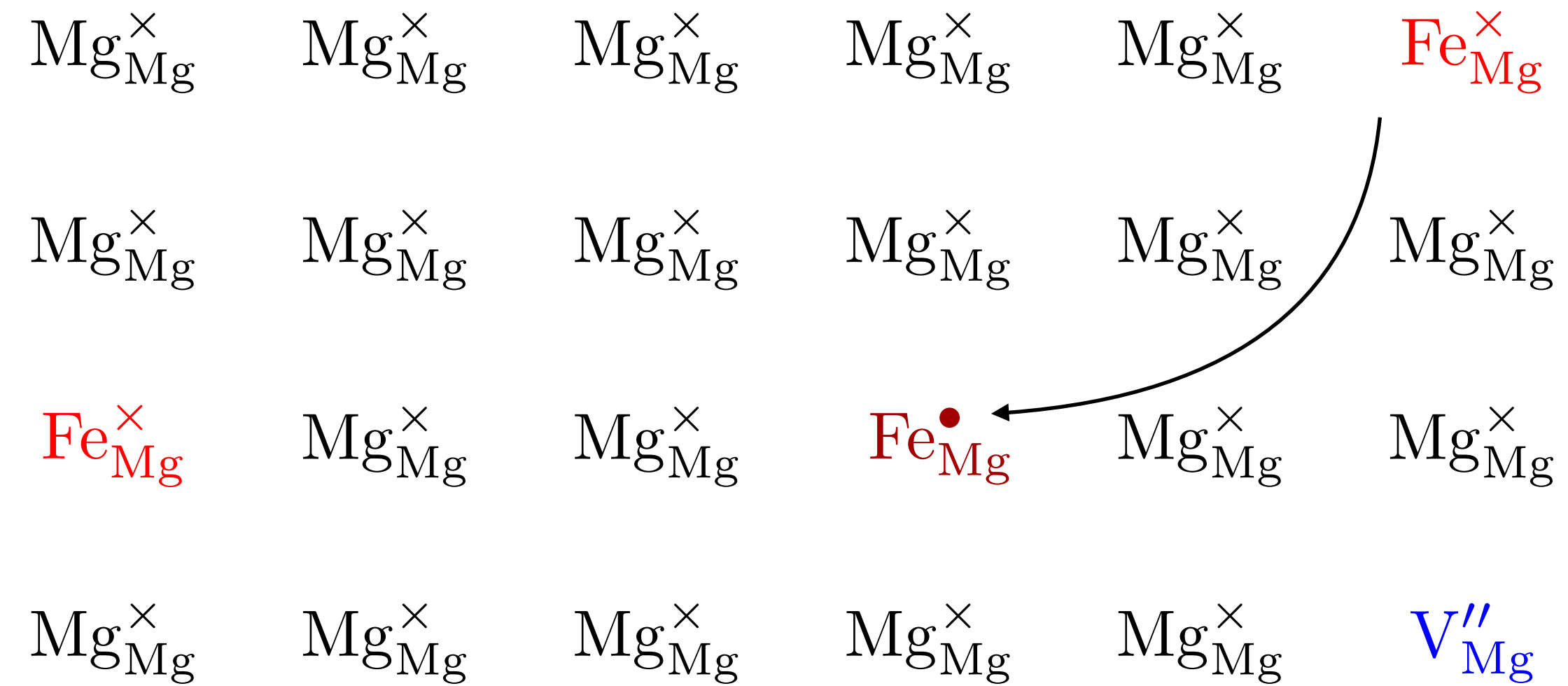
Polaron hopping



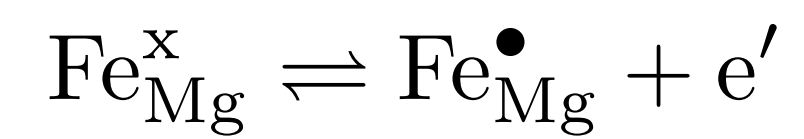
Oxidation of iron:



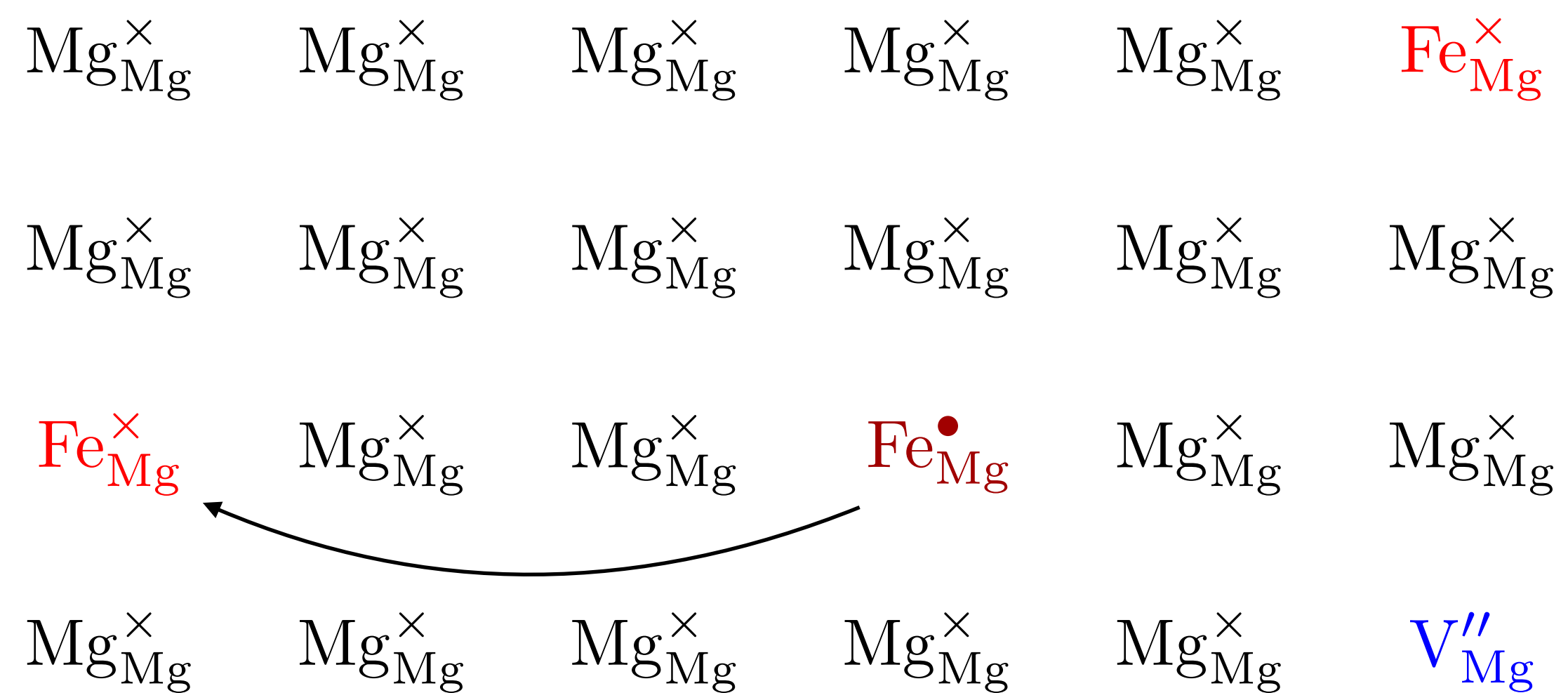
This effectively is movement of positive charge



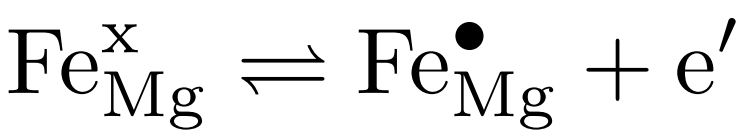
Oxidation of iron:



Polaron hopping



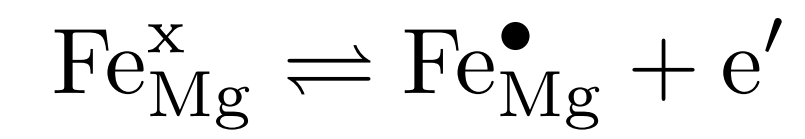
Oxidation of iron:



This effectively is movement of positive charge



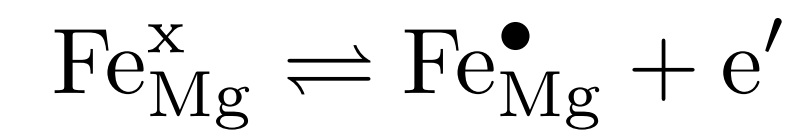
Oxidation of iron:



Similarly vacancies (Schottky defects) can move

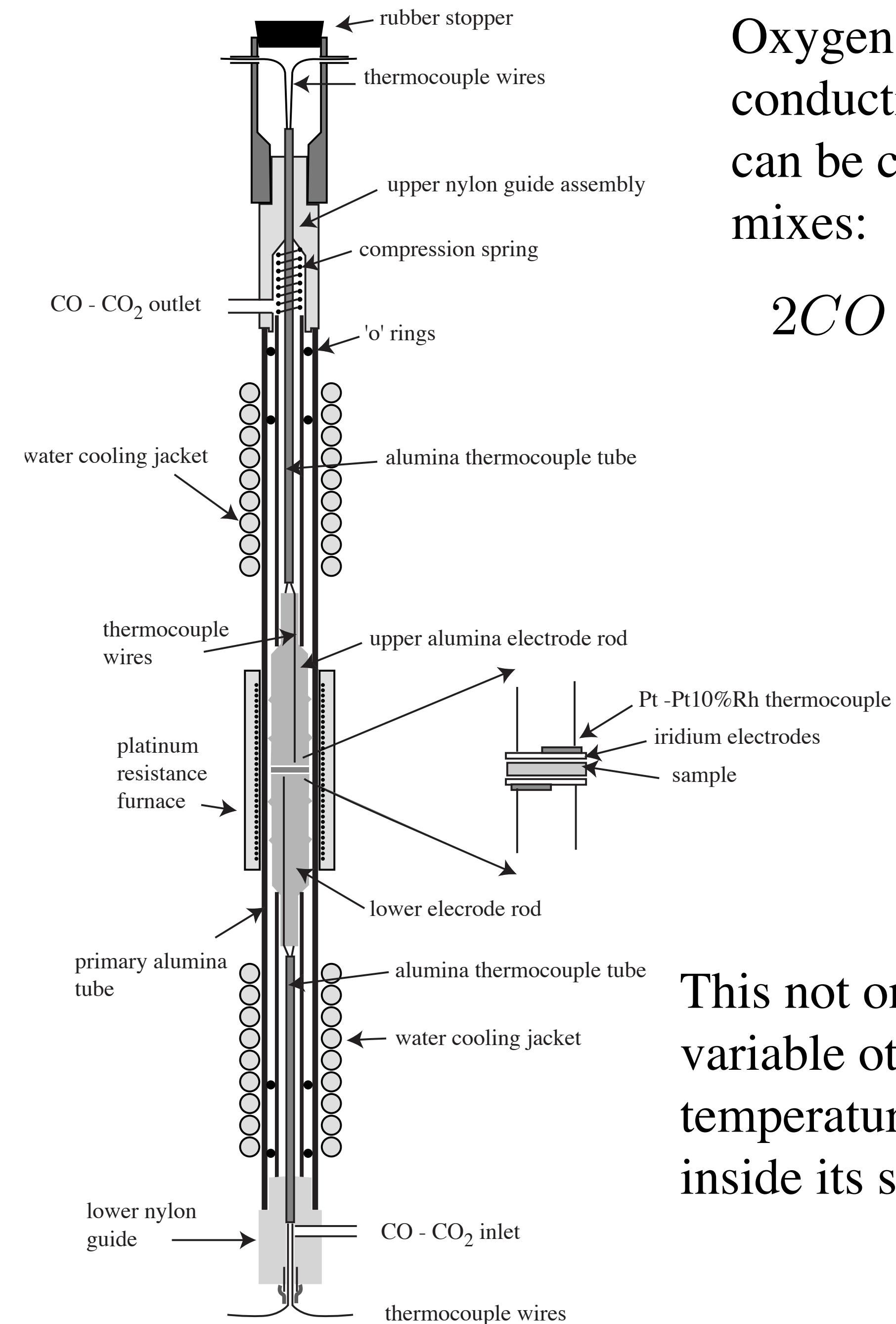


Oxidation of iron:

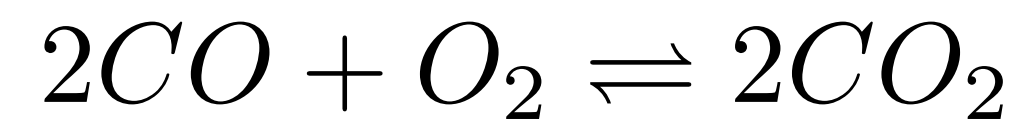


Effectively a movement of negative charge

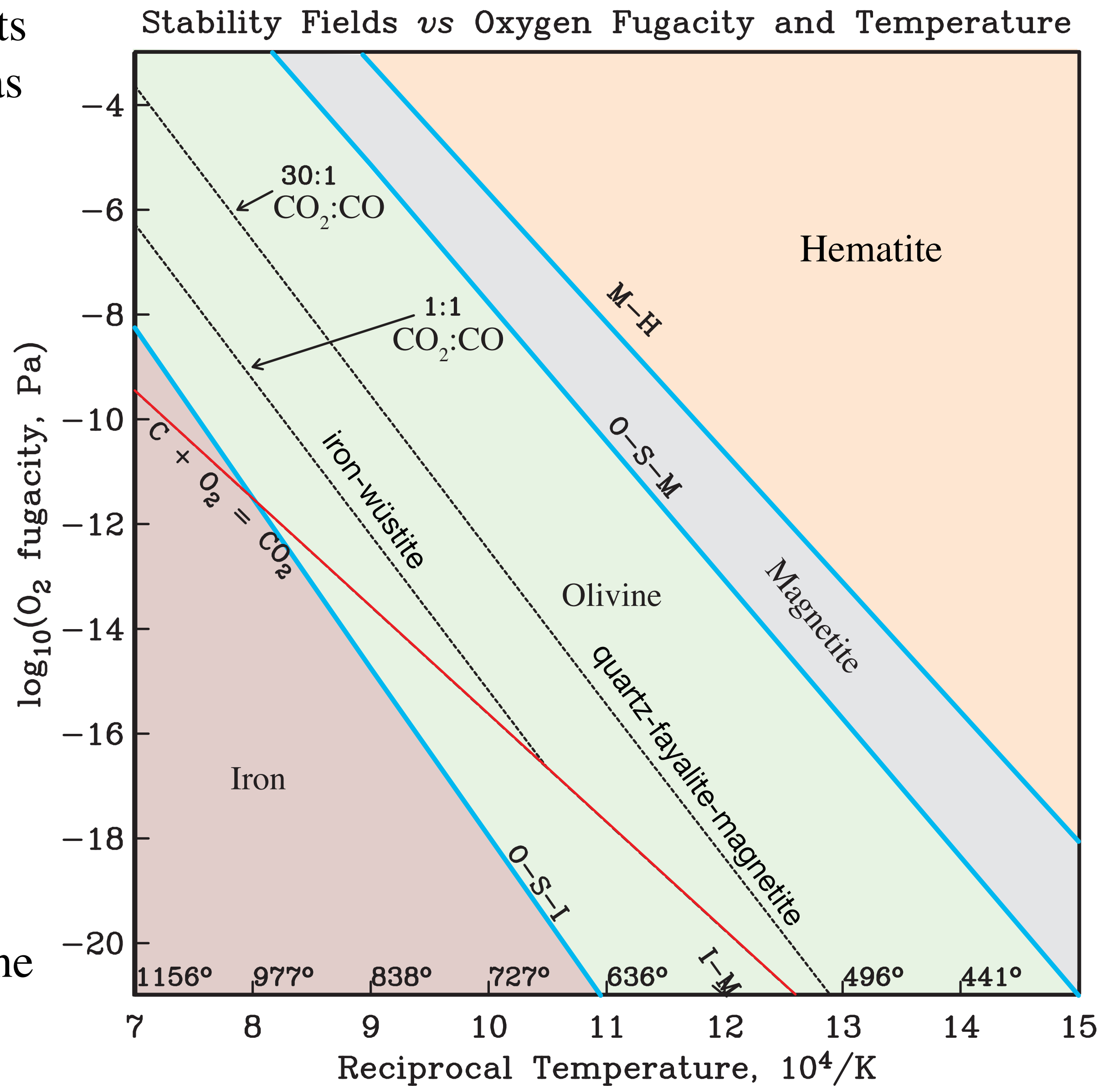




Oxygen activity during conductivity measurements can be controlled using gas mixes:

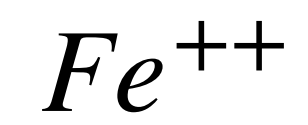


This not only provides a variable other than temperature, but keeps olivine inside its stability field.

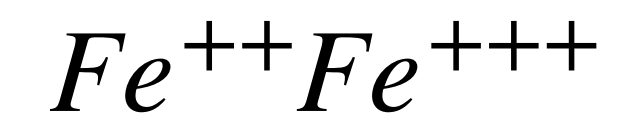
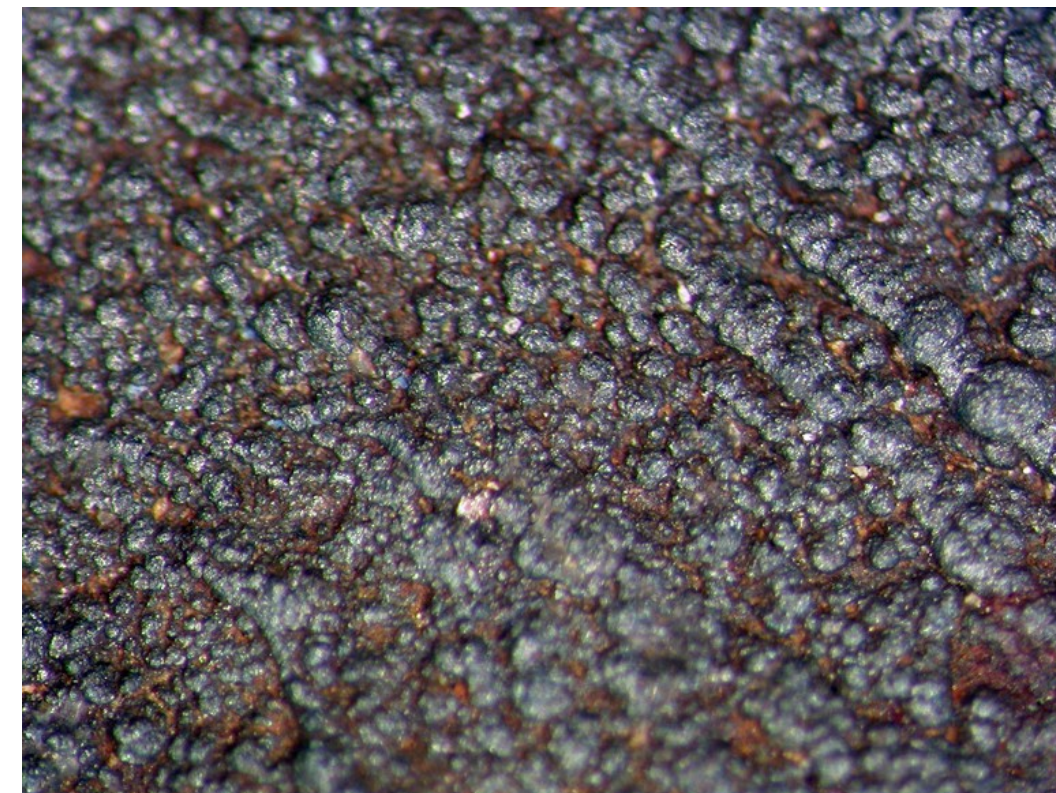




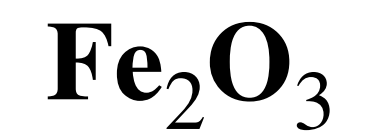
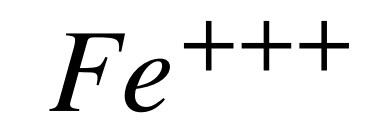
metallic iron



wüstite



magnetite

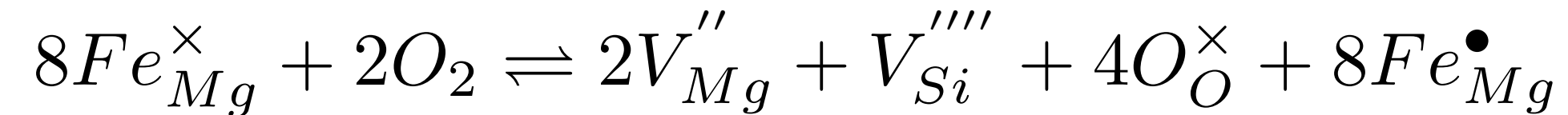


hematite

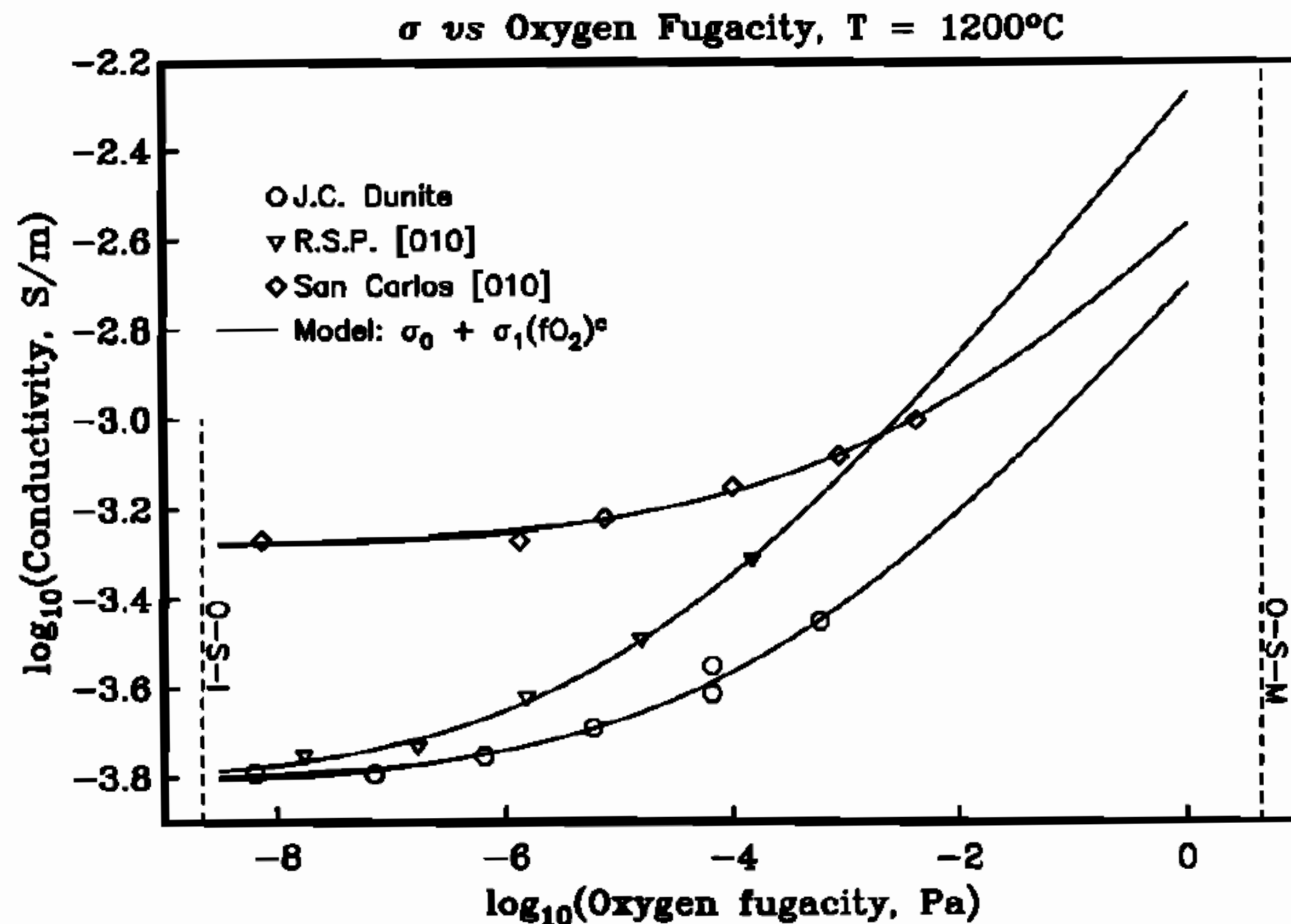


Images: Wikipedia

The oxidation of olivine ($\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_4$)



predicts that defect concentrations have a 1/6 power in oxygen fugacity $[X] = a_x f_{O_2}^{1/6}$

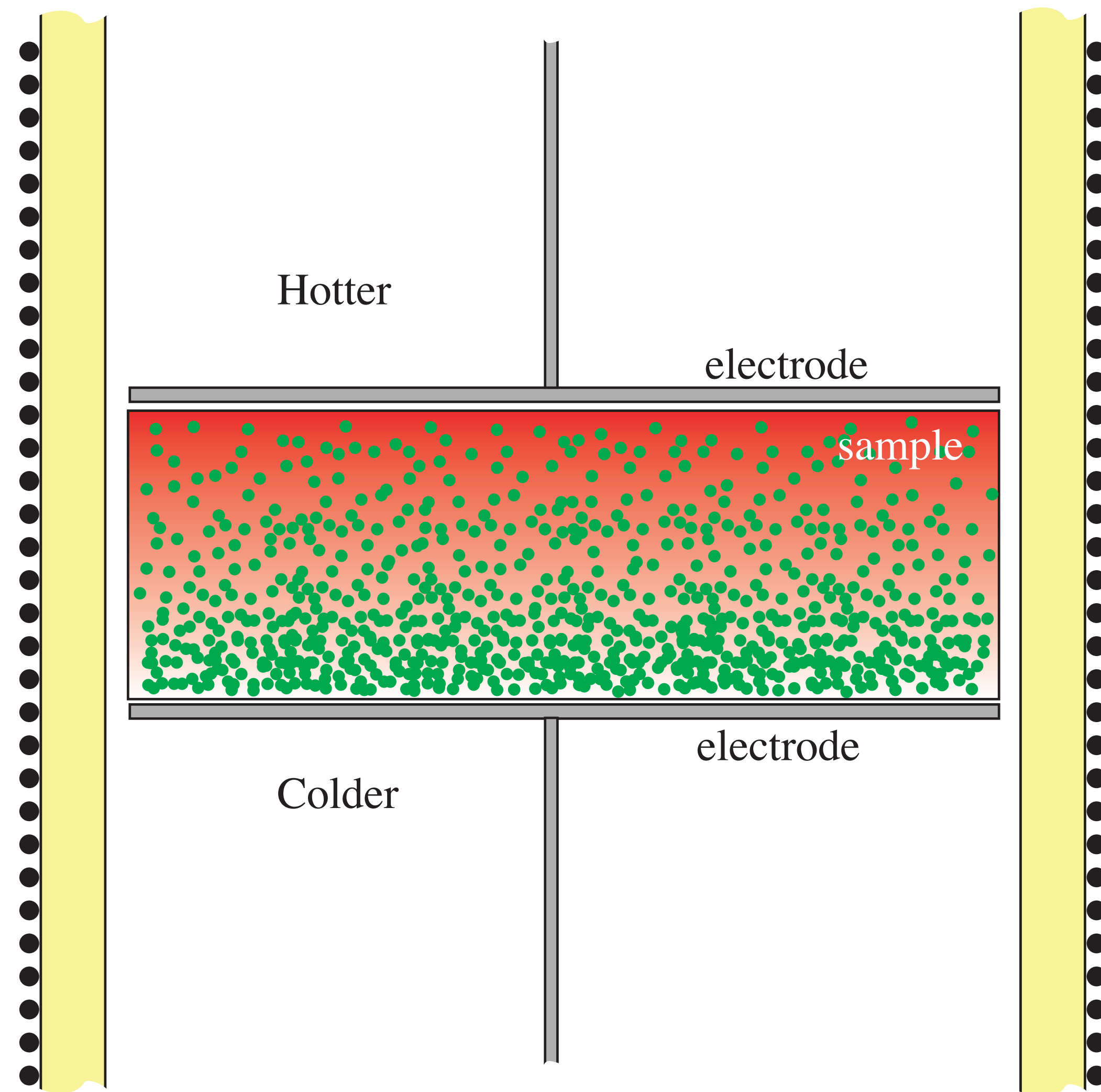


However, observed conductivity data require an additional term related to impurity defects and similar to doped conductivity

$$[X] = b_x + a_x f_{O_2}^{1/6}$$

(this could result from charge imbalances associated with impurity defects such as Al, Cr, Ti).

Thermo-electric power can also be used to estimate defect concentrations.



A temperature gradient ΔT across a mineral sample produces a potential difference ΔV as the charge carriers “condense” on the cold side. Thermopower, or Seebeck coefficient is defined as

$$Q = - \lim_{\Delta T \rightarrow 0} \frac{\Delta V}{\Delta T}$$

The sign of the thermopower is the same as the sign of the charge carriers, and depends on relative concentration, c :

$$Q = \frac{k}{q} \left[\ln \beta \frac{(1 - c)}{c} + \frac{S}{k} \right]$$

A change in sign in the Seebeck coefficient at 1400° C was documented in Schock, Duba, and Shankland's seminal 1989 paper.

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 94, NO. B5, PAGES 5829–5839, MAY 10, 1989

Electrical Conduction in Olivine

ROBERT N. SCHOCK

Energy Program, University of California, Lawrence Livermore National Laboratory, Livermore

ALFRED G. DUBA

Earth Sciences Department, University of California, Lawrence Livermore National Laboratory, Livermore

THOMAS J. SHANKLAND

Geophysics Group, University of California, Los Alamos National Laboratory, Los Alamos, New Mexico

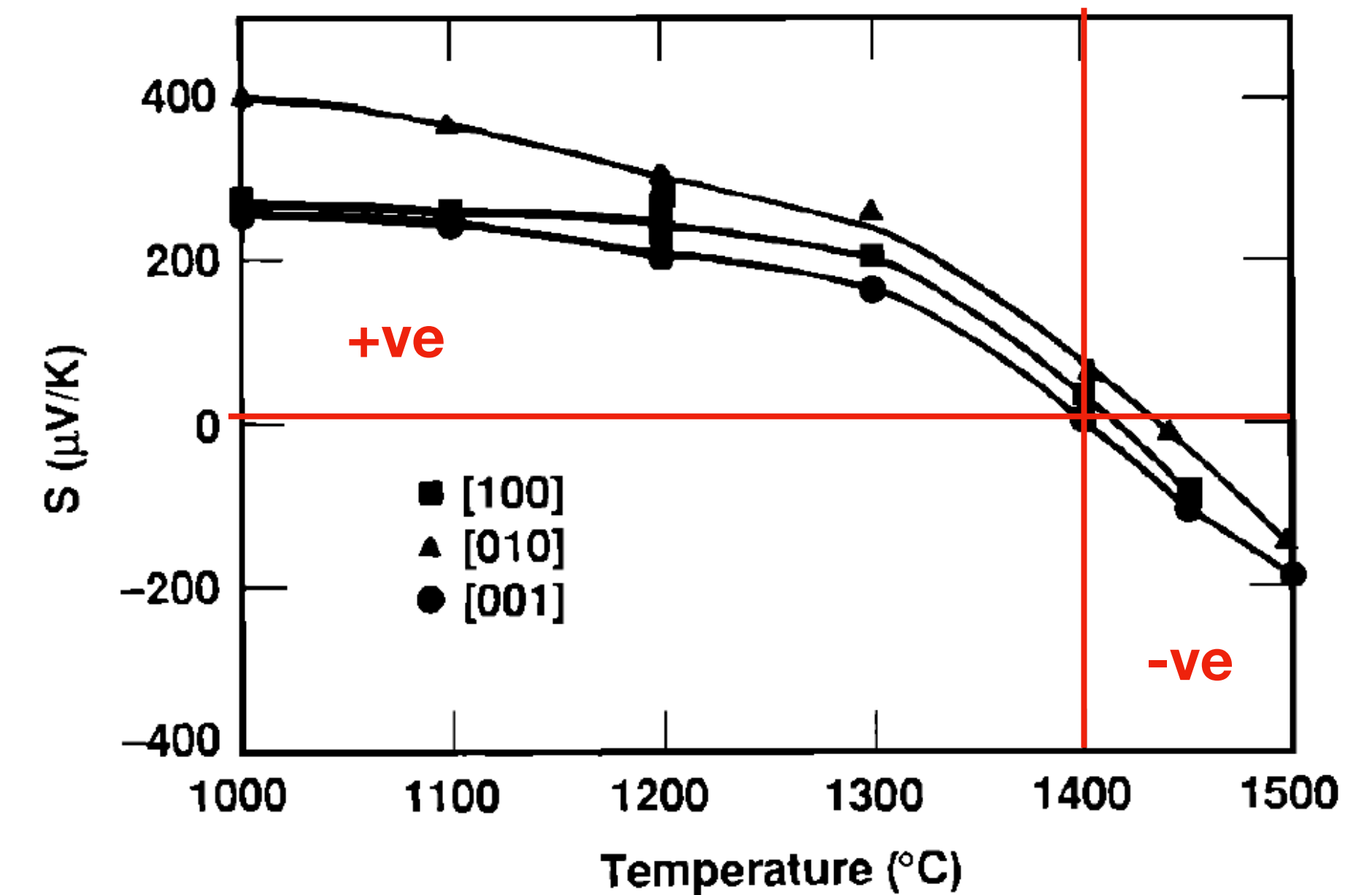
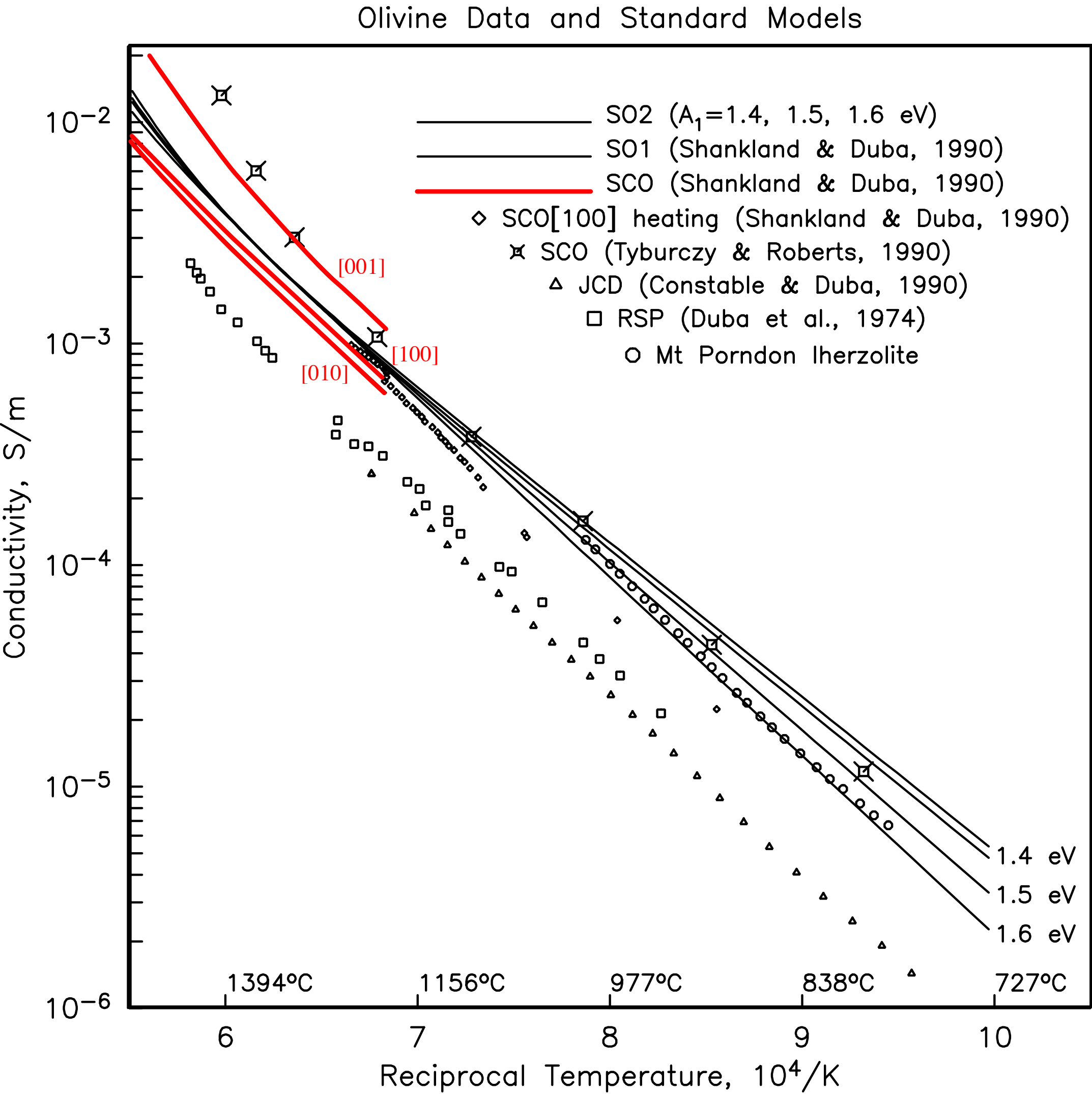


Fig. 9. Thermoelectric coefficient S of San Carlos olivine as a function of temperature along the three principal crystallographic axes. $P_{\text{O}_2} = 10^{-4}$ Pa (1200 $^{\circ}\text{C}$).

They interpreted this a change in conduction from electron holes at low temperature to magnesium vacancies at high temperature.

Standard olivine models:



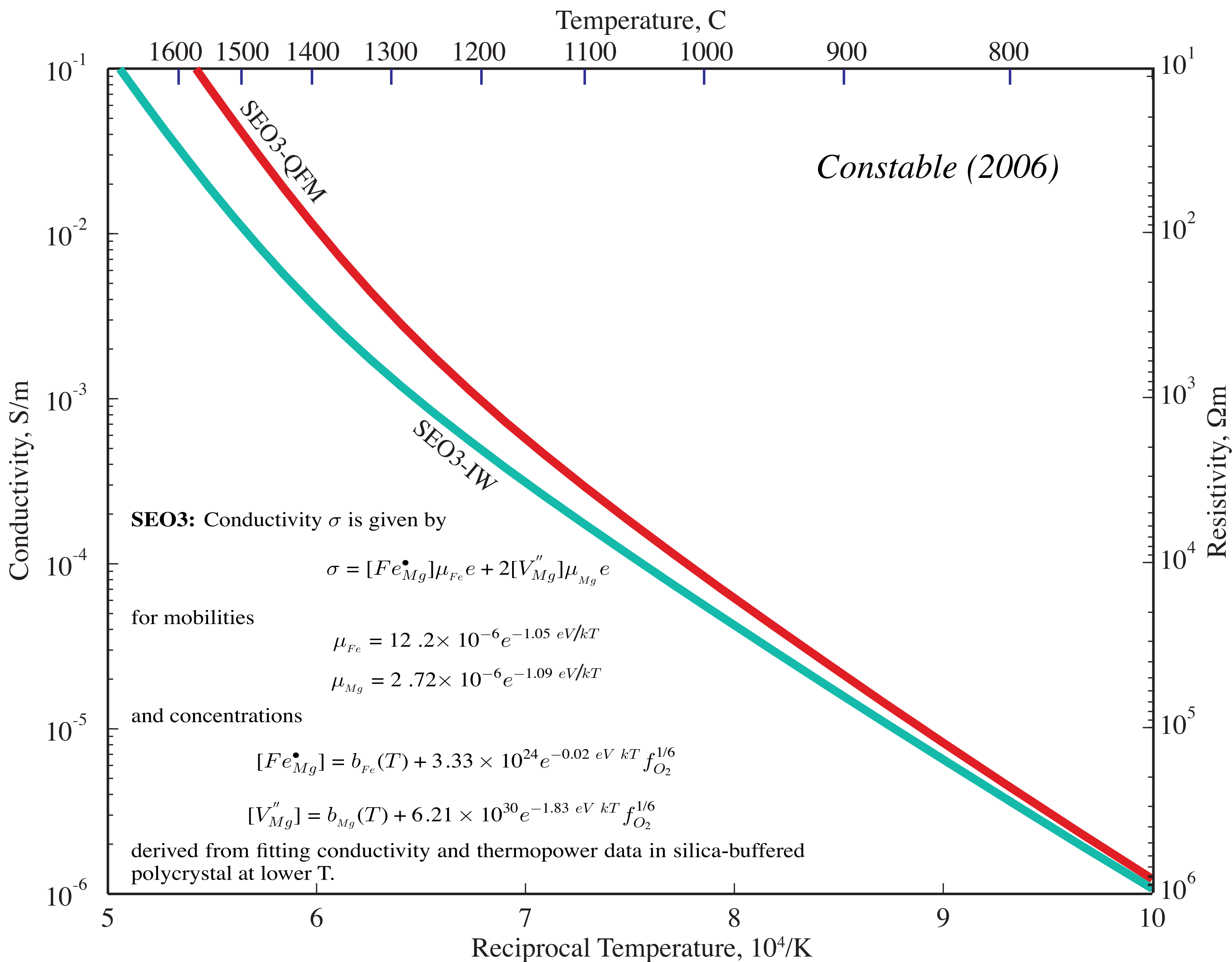
SO1: *Shankland and Duba (1990)*

$$\sigma = 10^{1.67} e^{-1.38\text{eV}/kT} + 10^{8.7} e^{-3.90\text{eV}/kT} \text{ S/m}$$

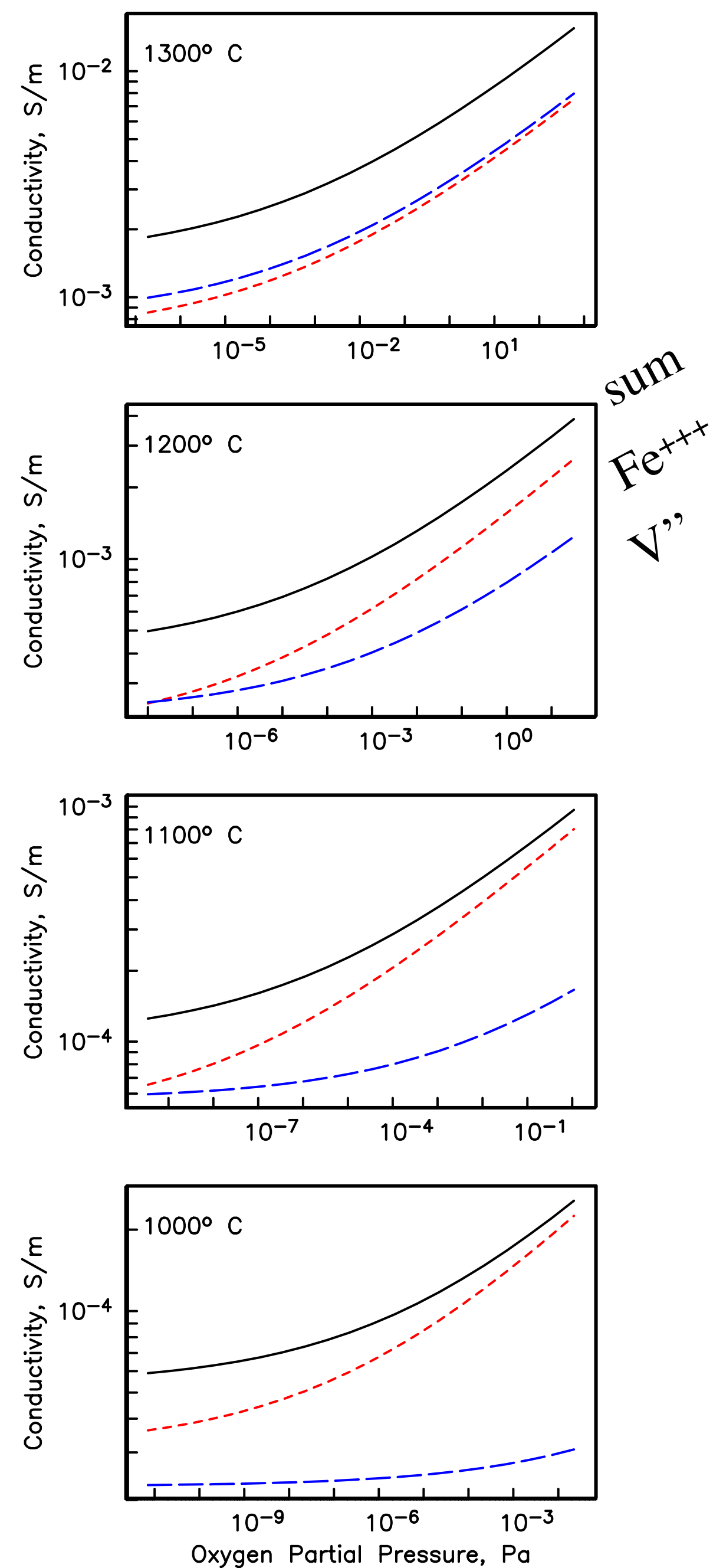
SO2: *Constable, Shankland and Duba (1992)*

$$\sigma = 10^{2.40} e^{-1.6\text{eV}/kT} + 10^{9.17} e^{-4.25\text{eV}/kT} \text{ S/m}$$

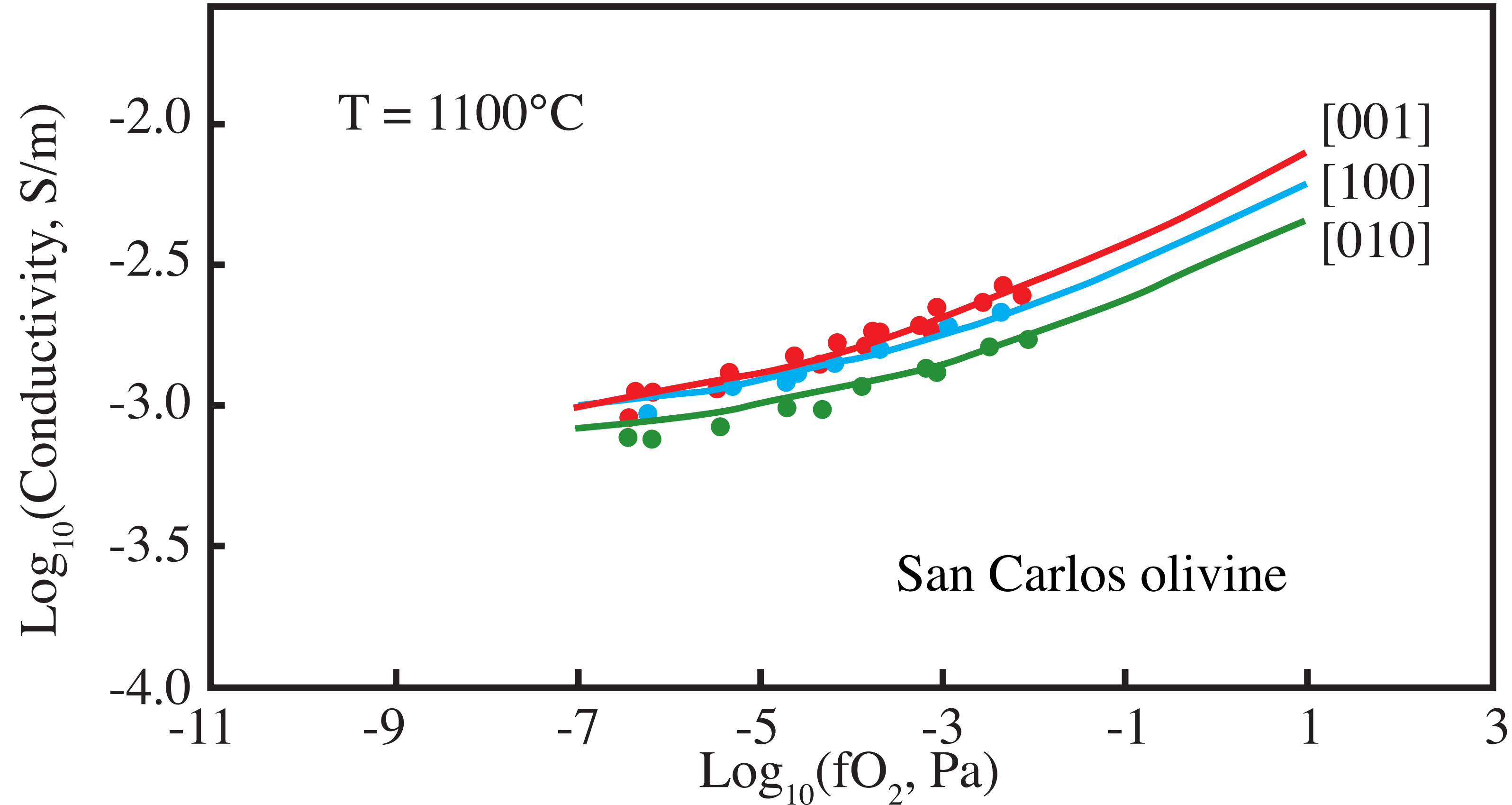
SEO3 (Standard Electrical Olivine #3):



Constable and Roberts (1997)

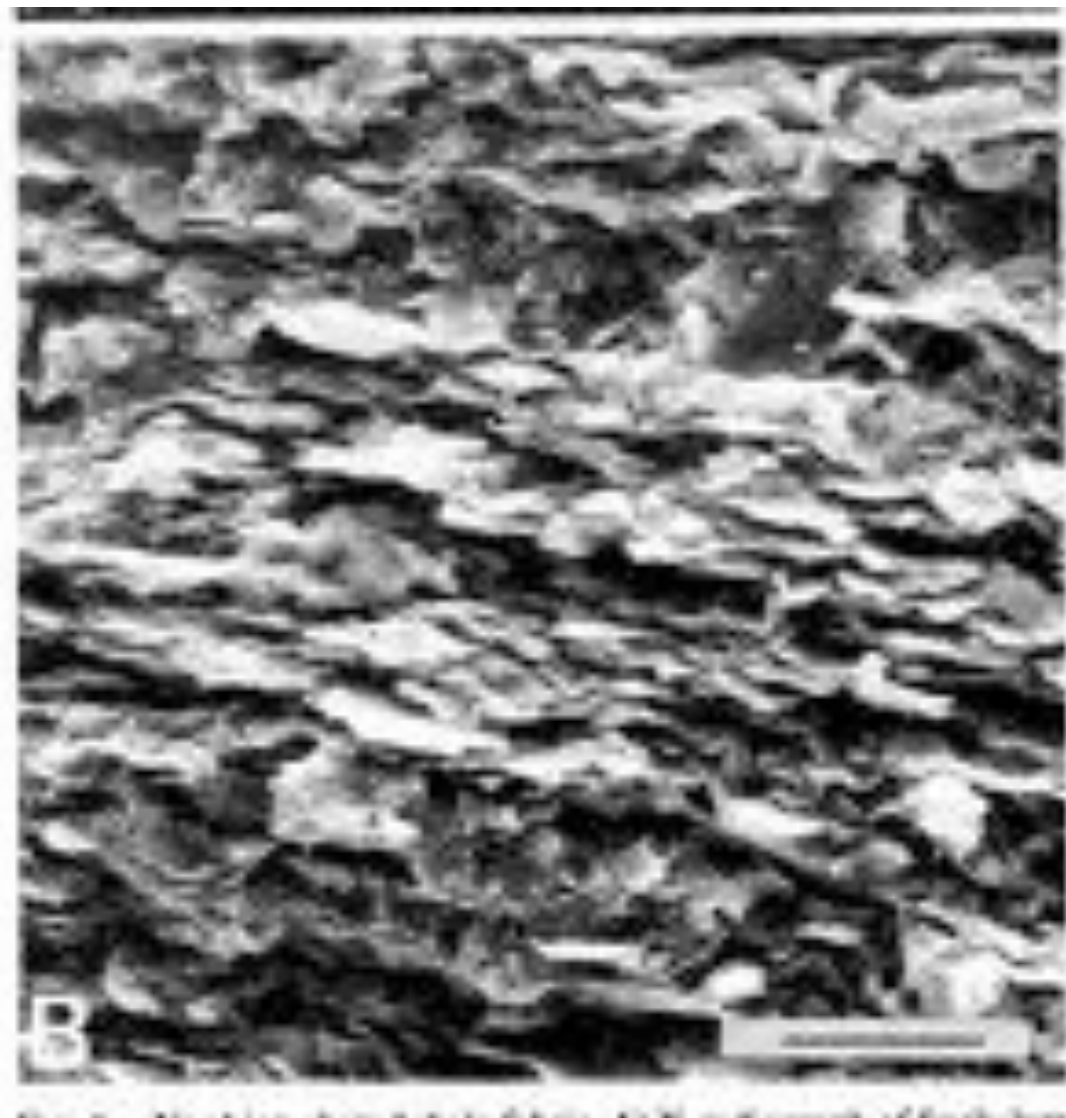
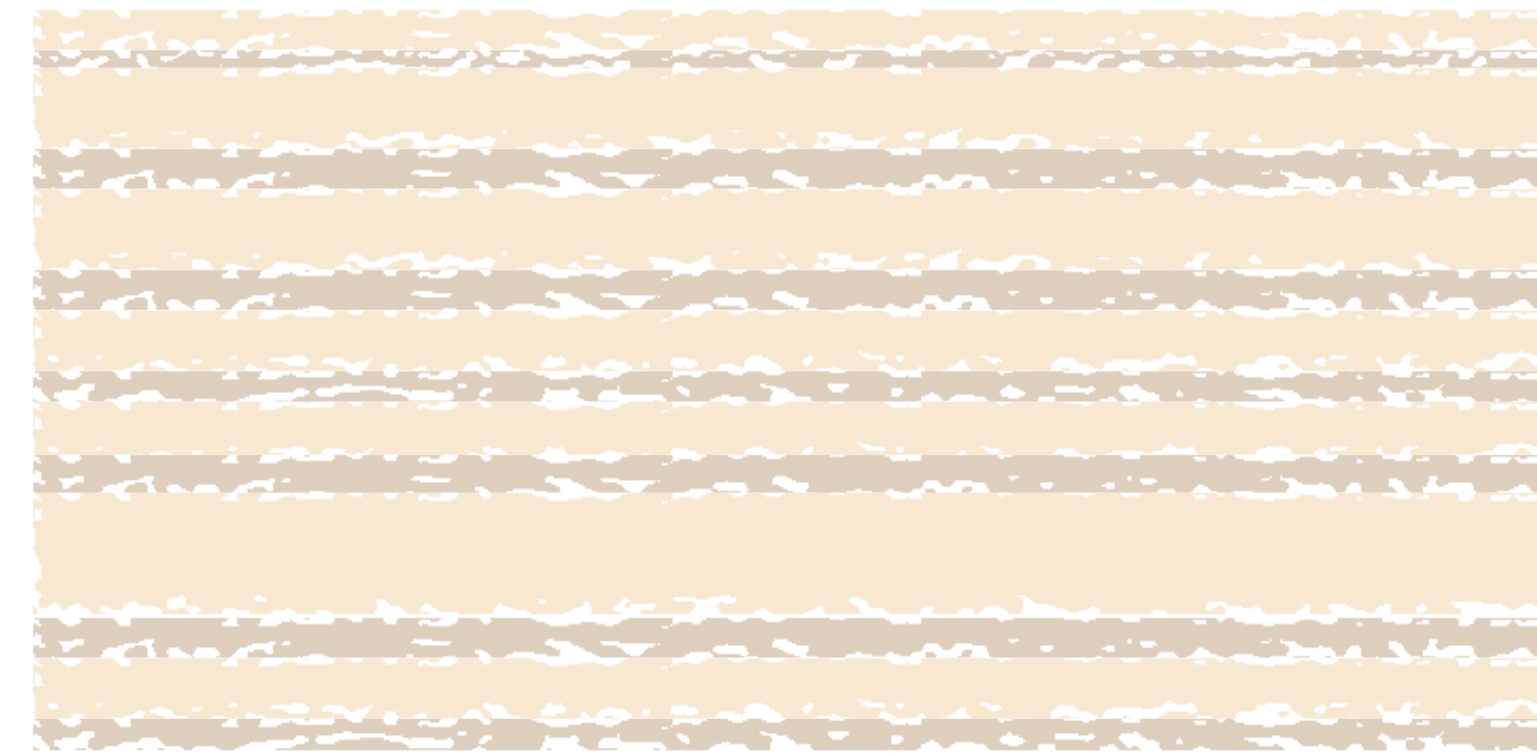
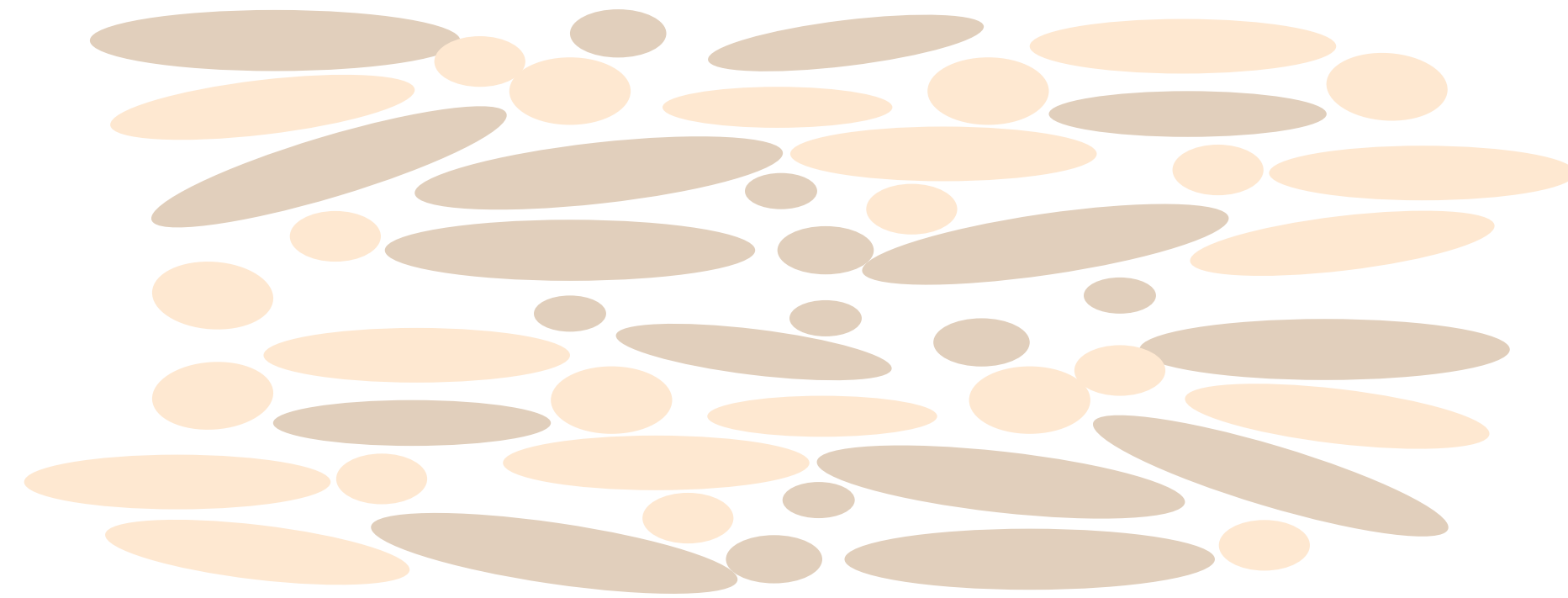


Anisotropy results when conductivity varies with direction. It can occur at the crystal level.

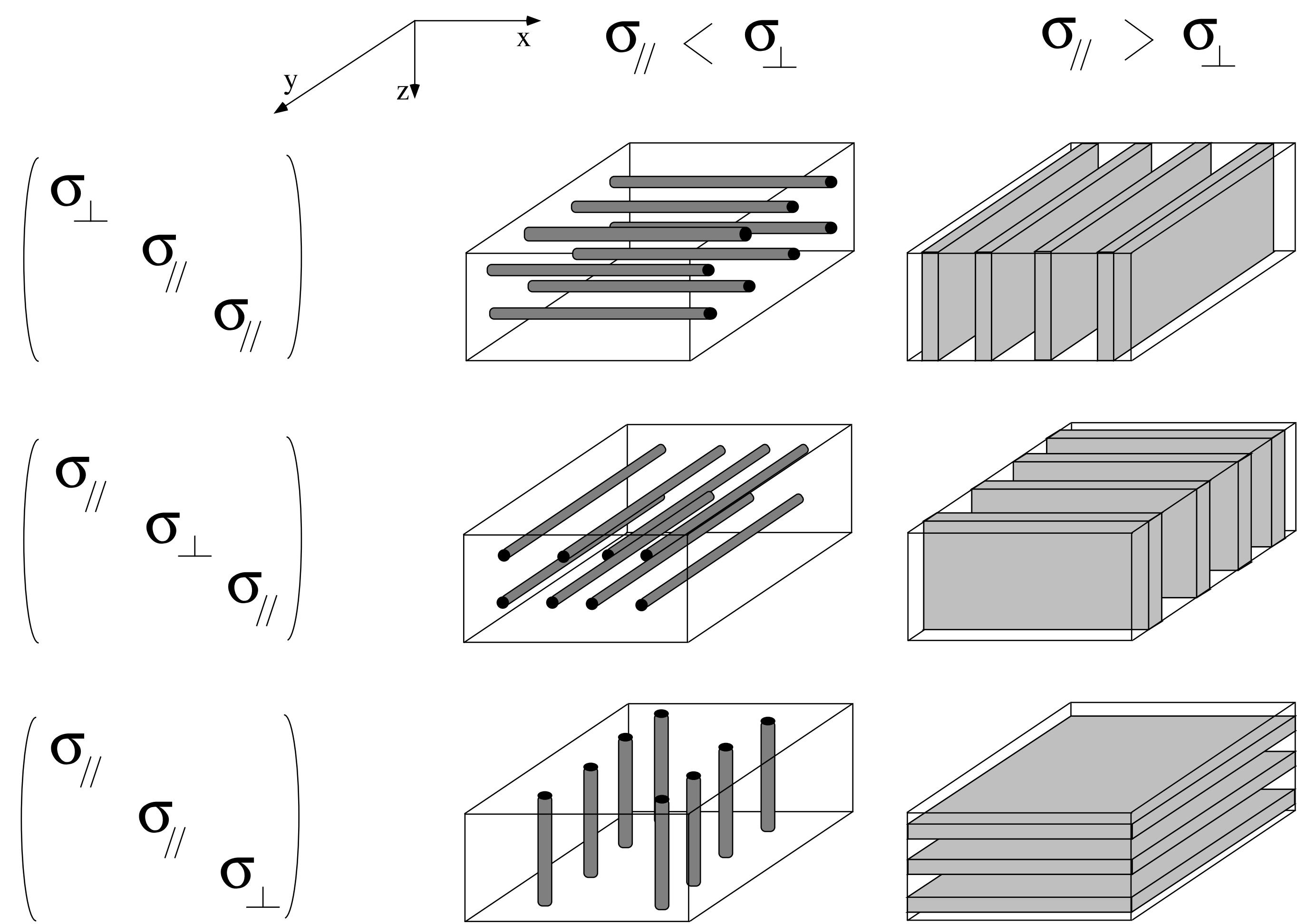


Anisotropy: Aligned crystals and interbedding can produce anisotropy on microscopic to macroscopic scales. Because of gravity, in undeformed sedimentary rock the orientation is sub-horizontal, resulting in higher resistivities in the vertical direction than the horizontal direction.

EM cannot tell micro from macro anisotropy until the layers get very thick.

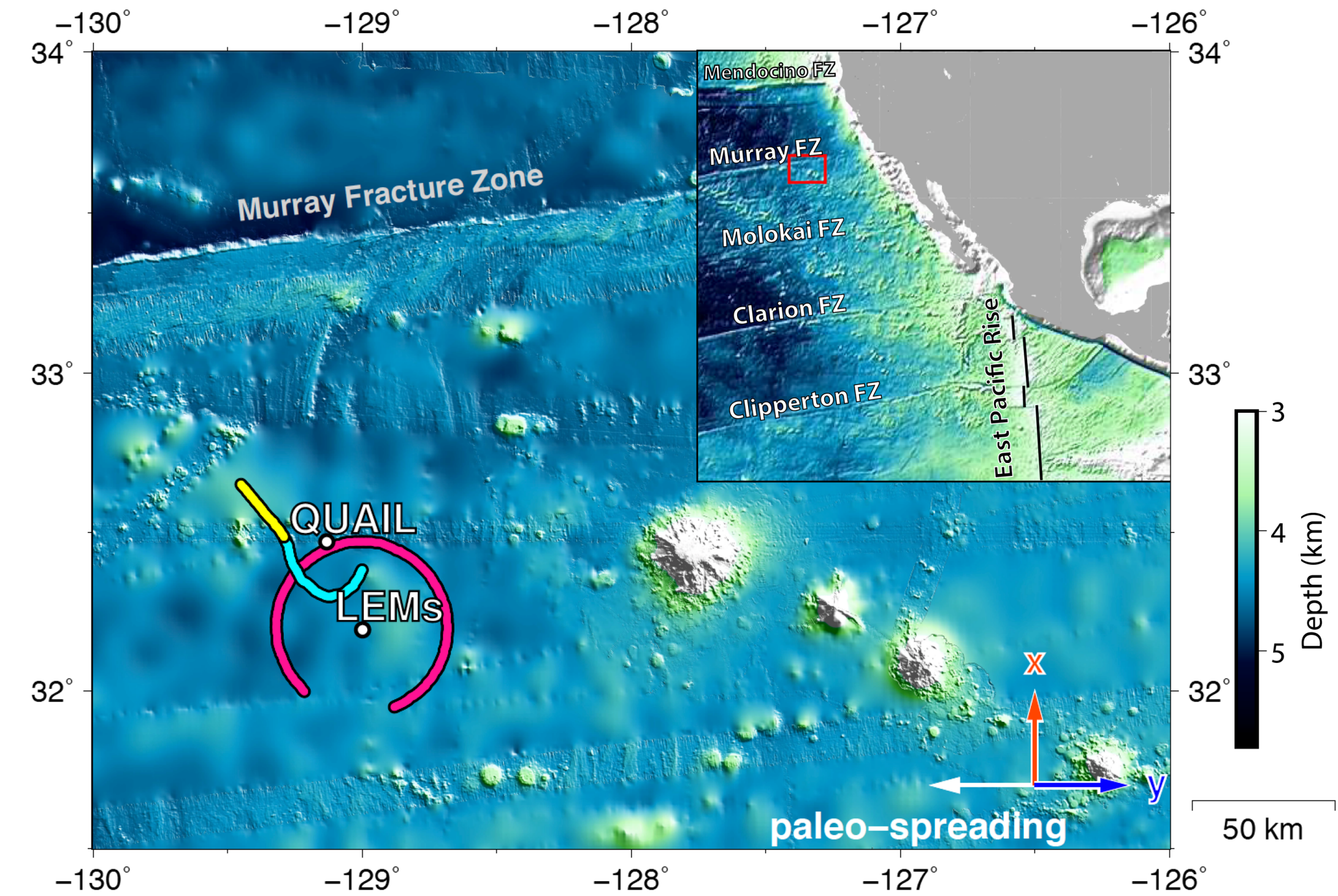
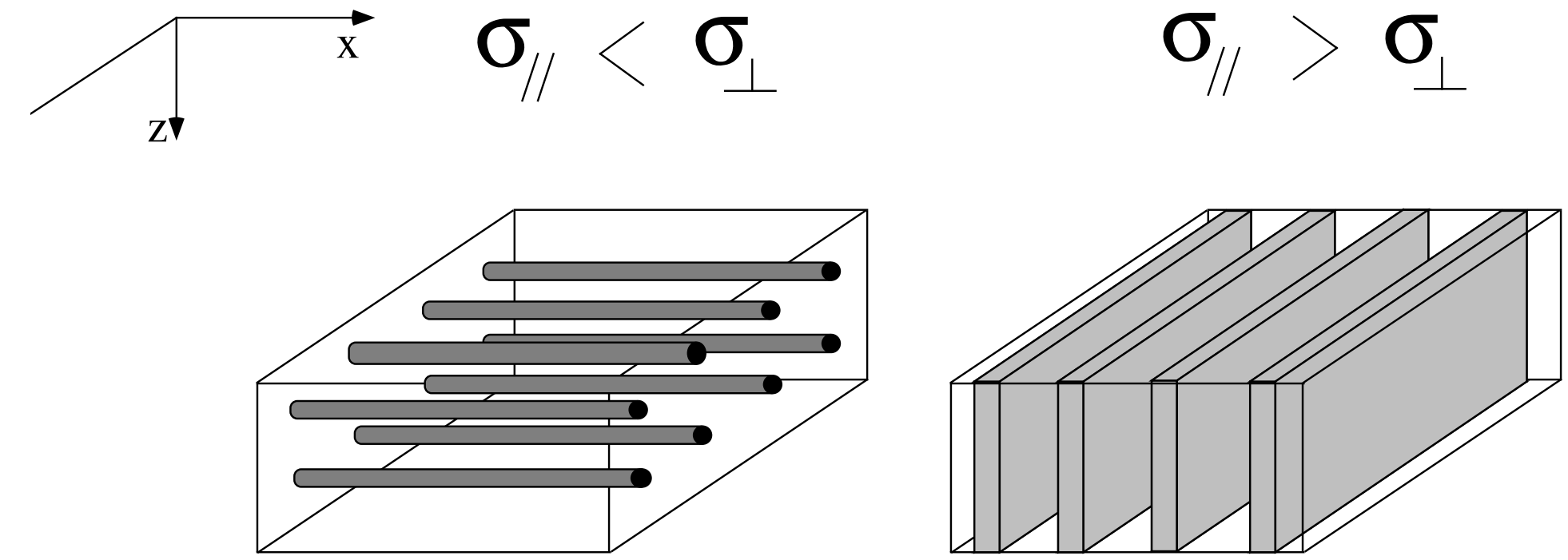
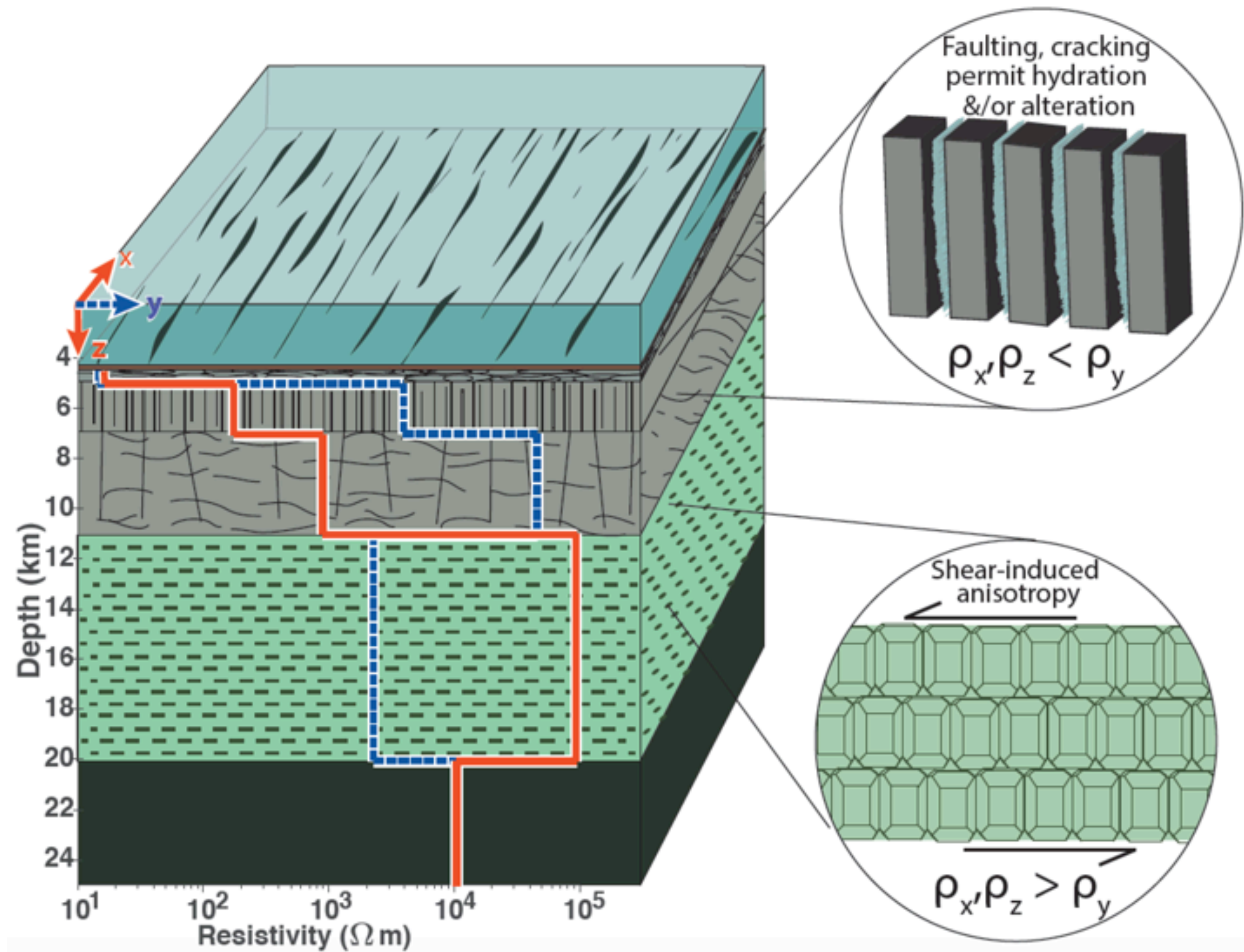


In general all three axes can be different (and not even orthogonal), but many geological systems are *transversely isotropic*:



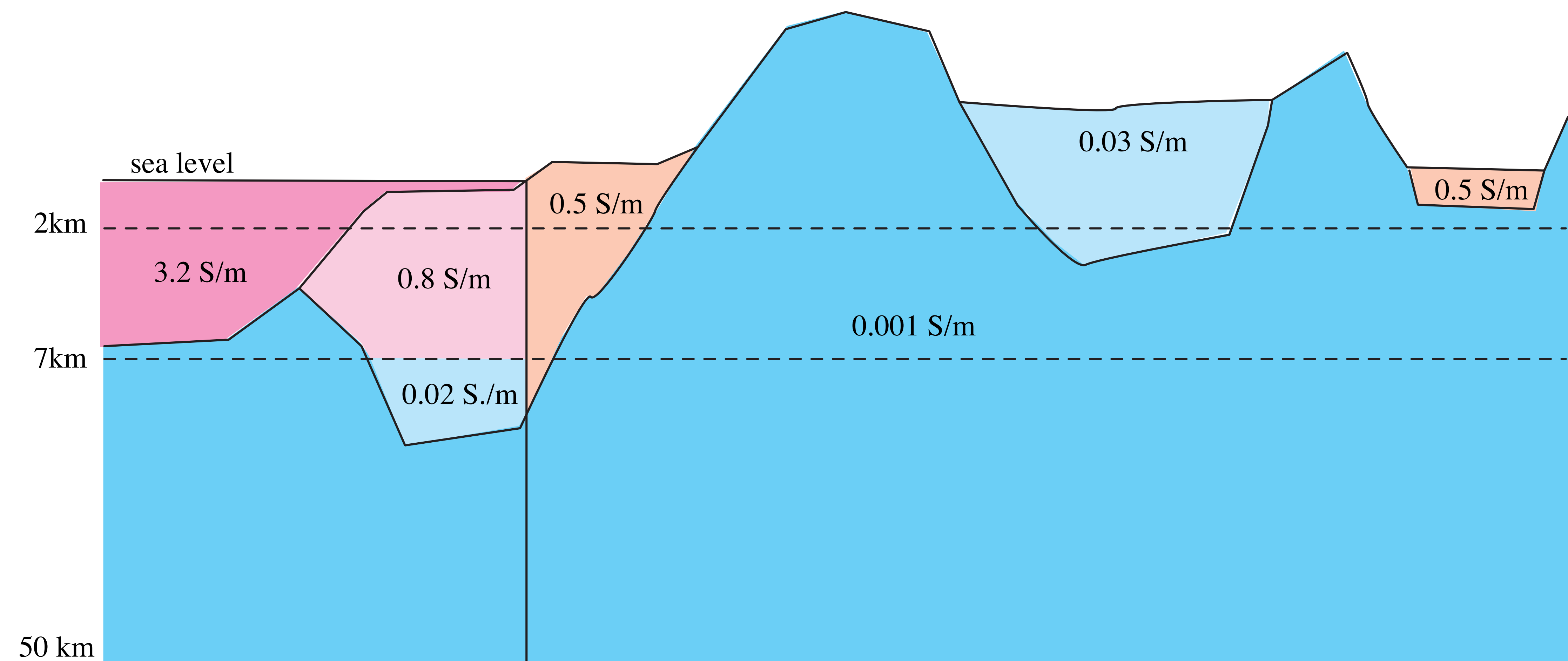
Conductors = grey.

Some recent work:

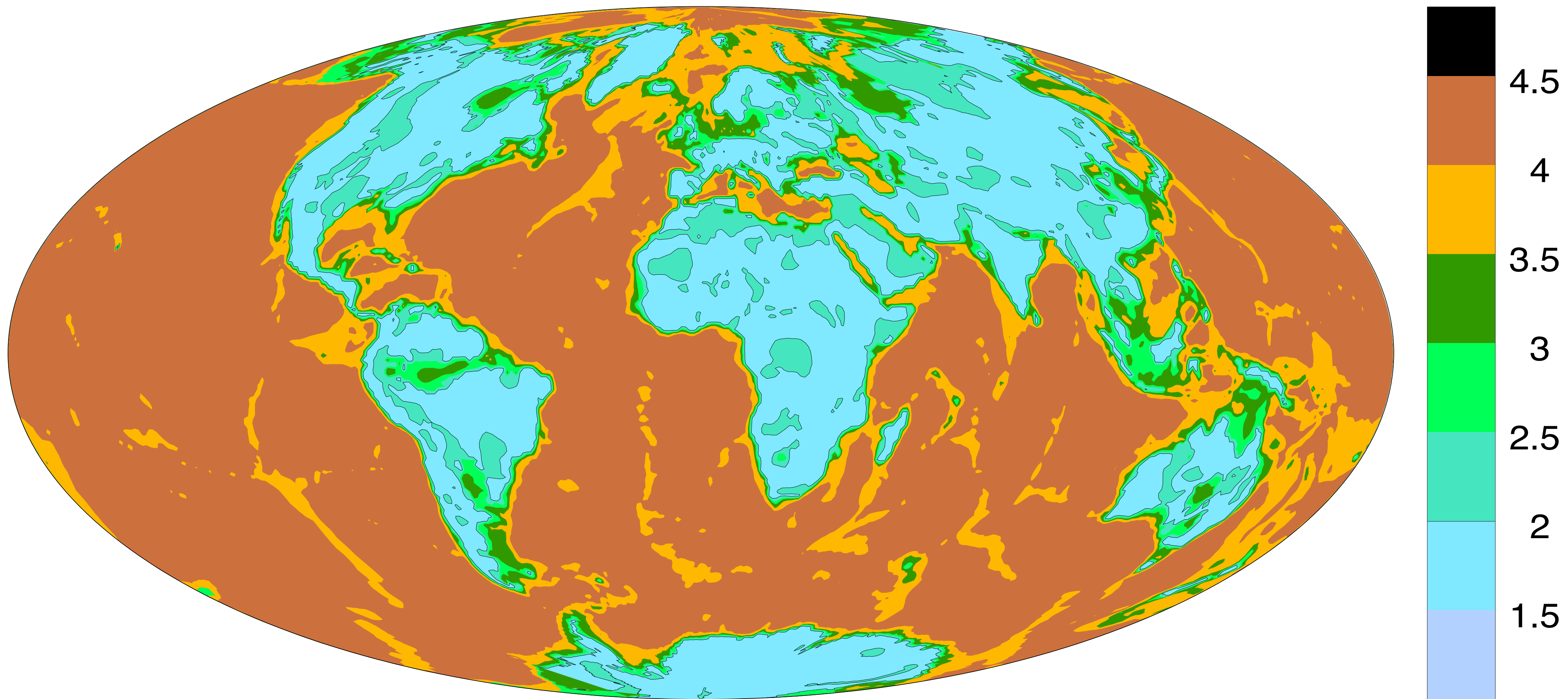


Chesley et al. (2019)

A crustal conductivity model:

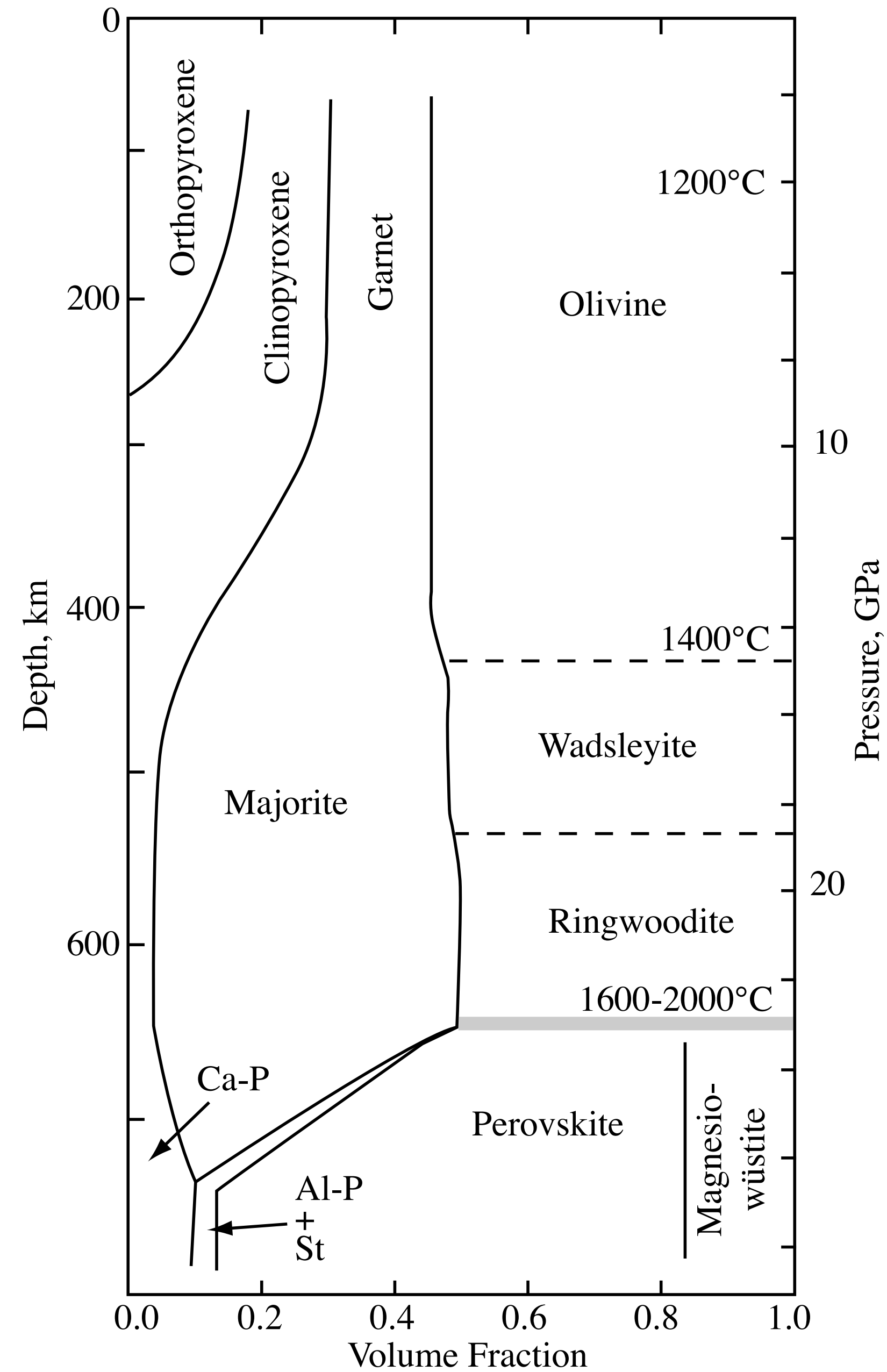
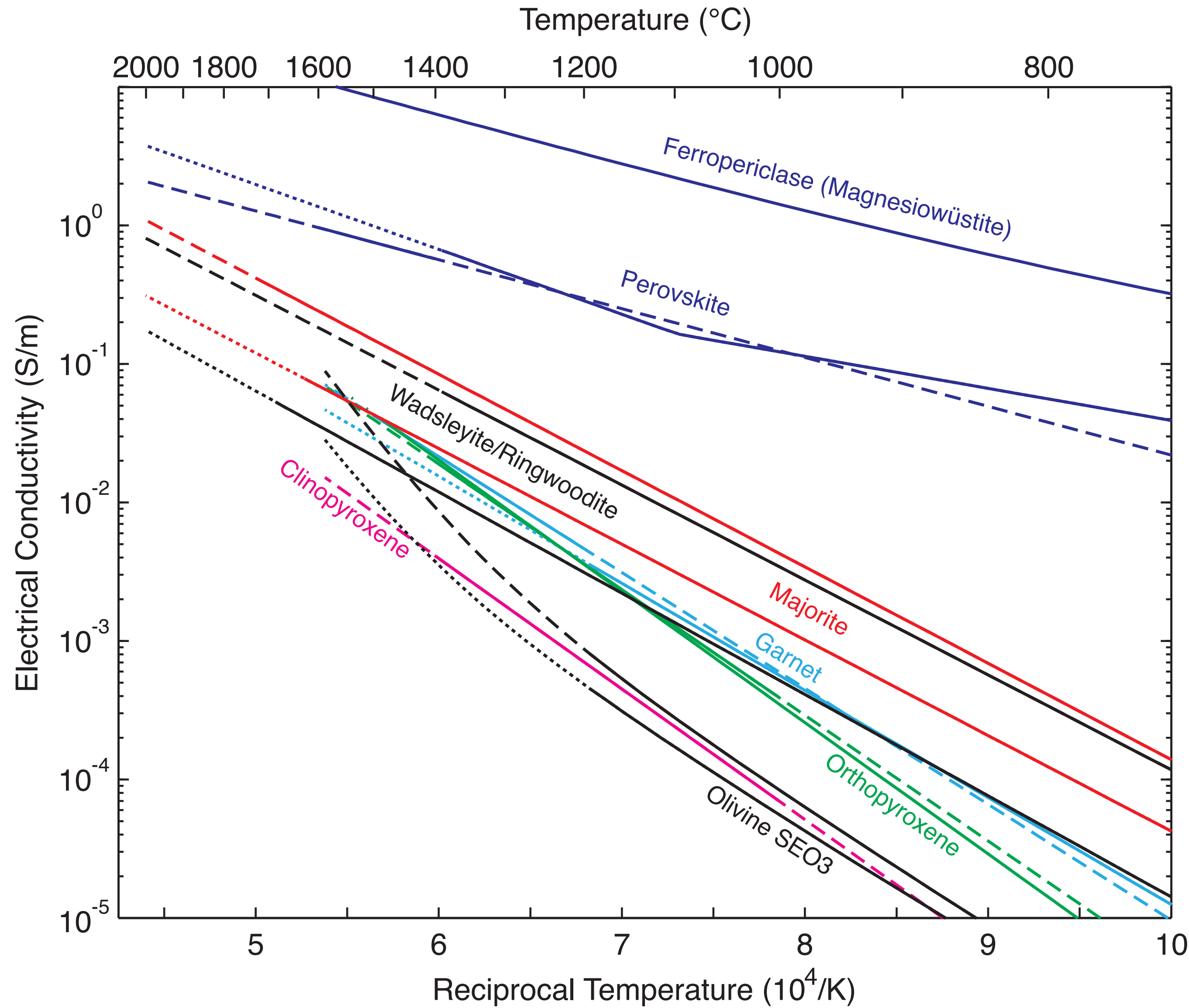


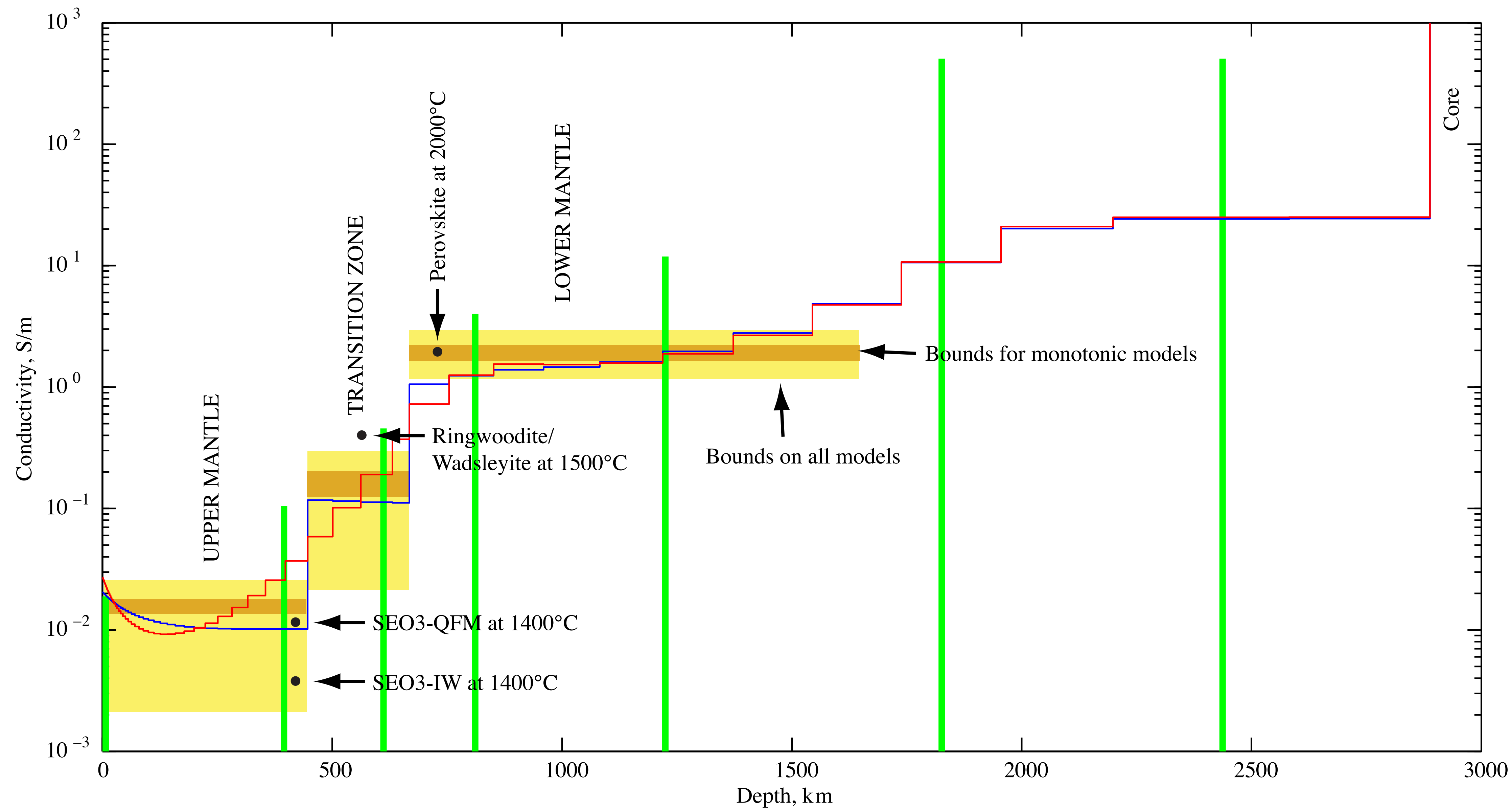
global surface conductance map, logarithmic scale [$\log_{10} S$]



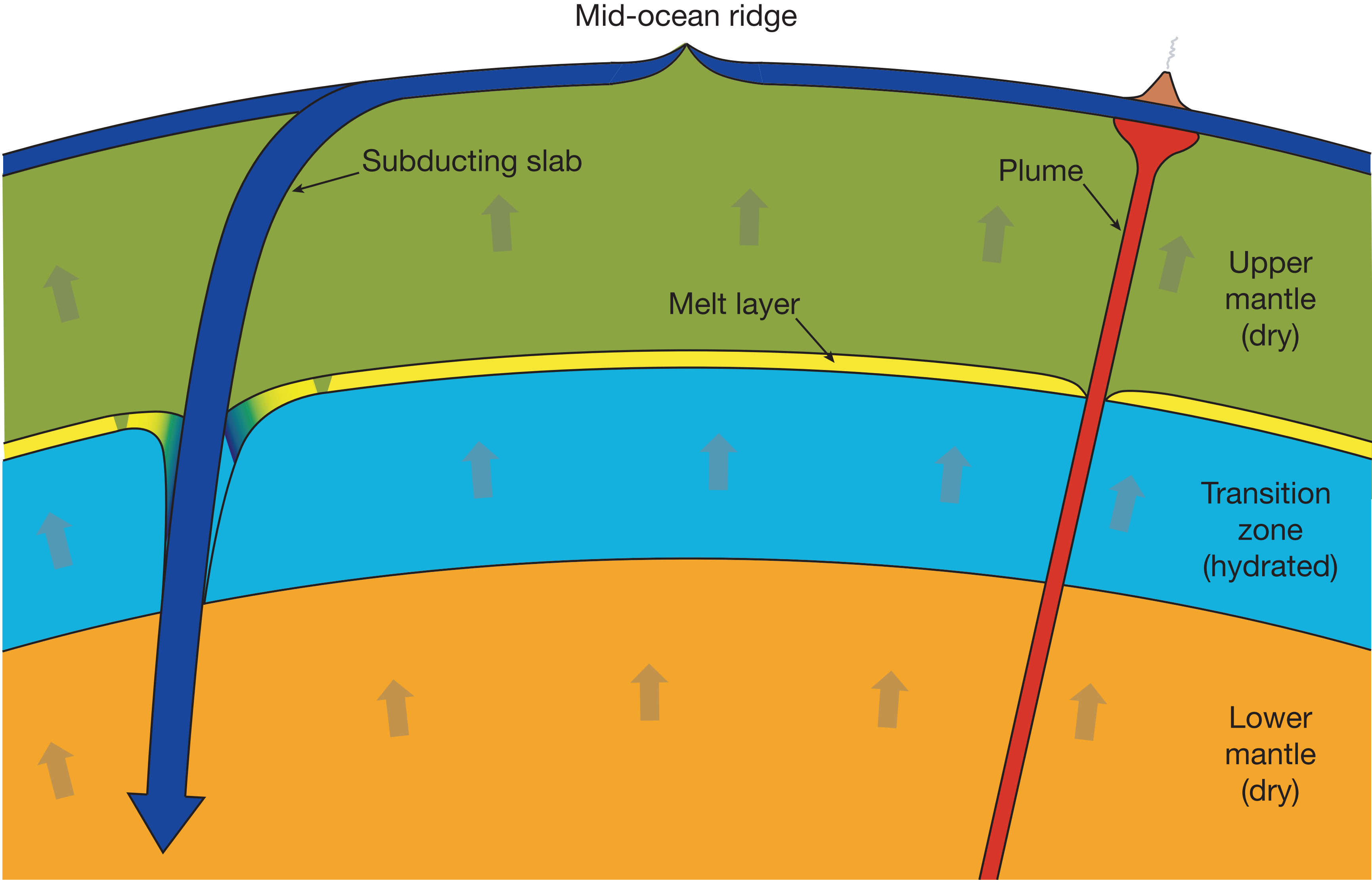
Everett and Constable² (2003)

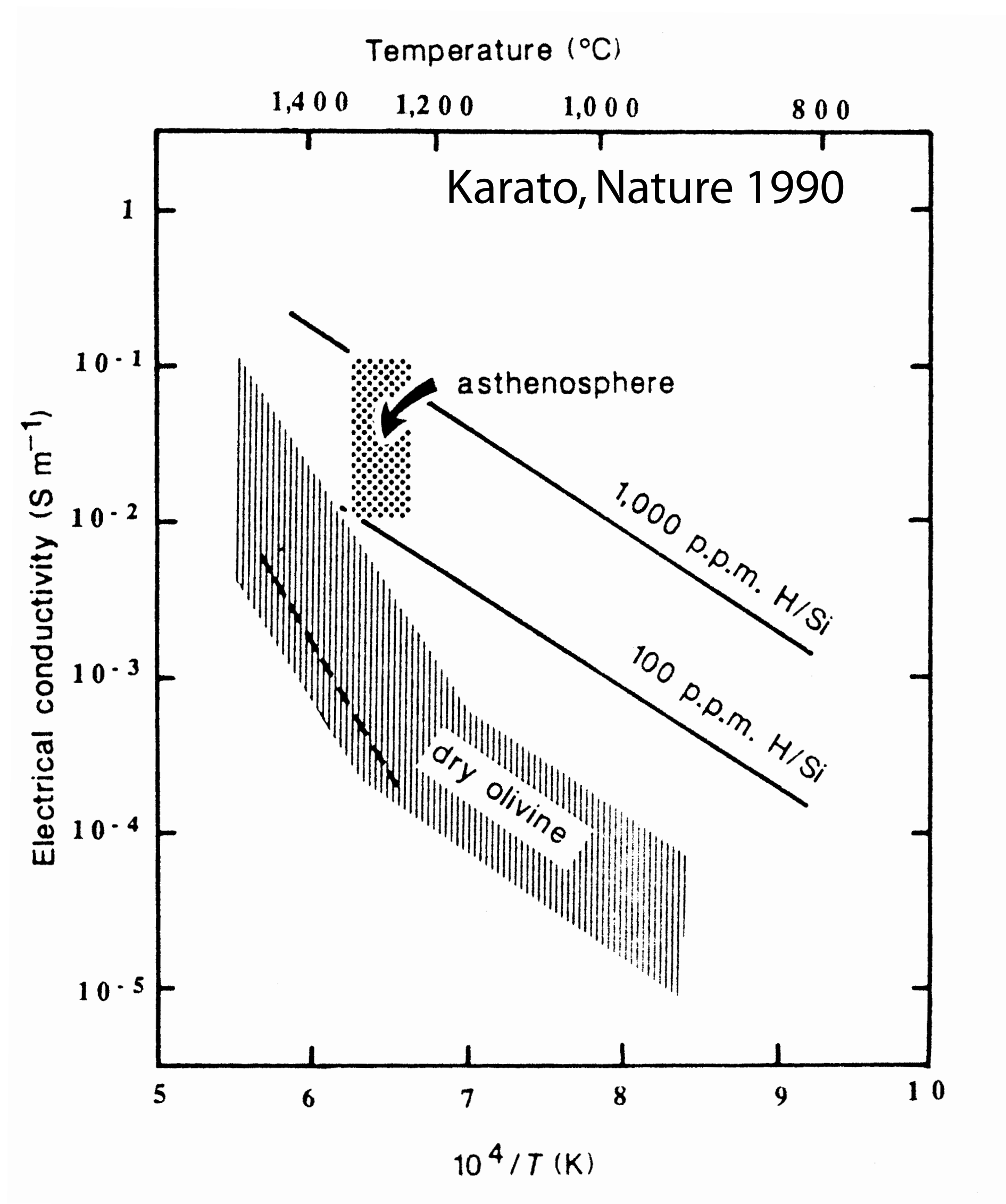
A dry mantle model:

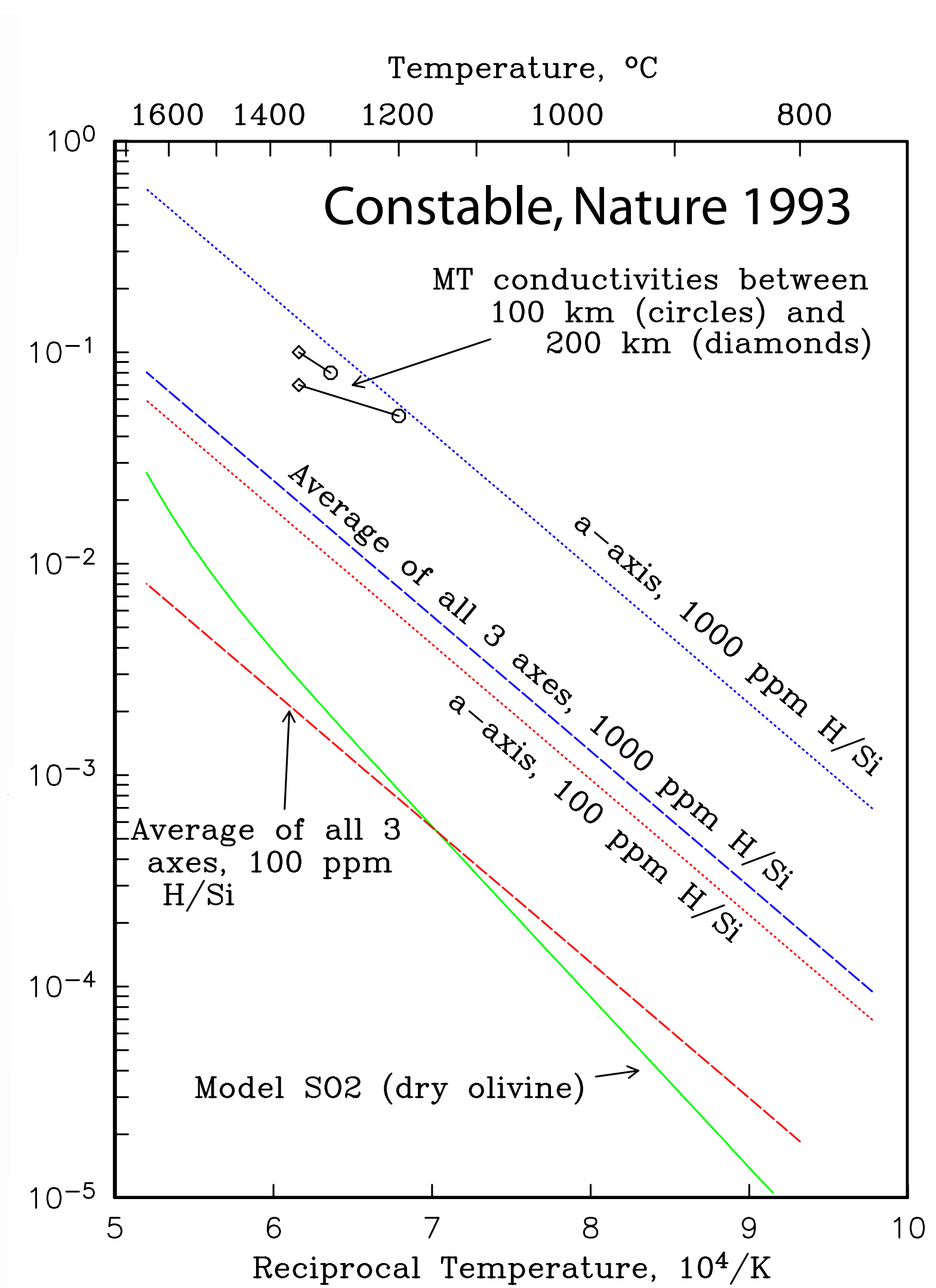
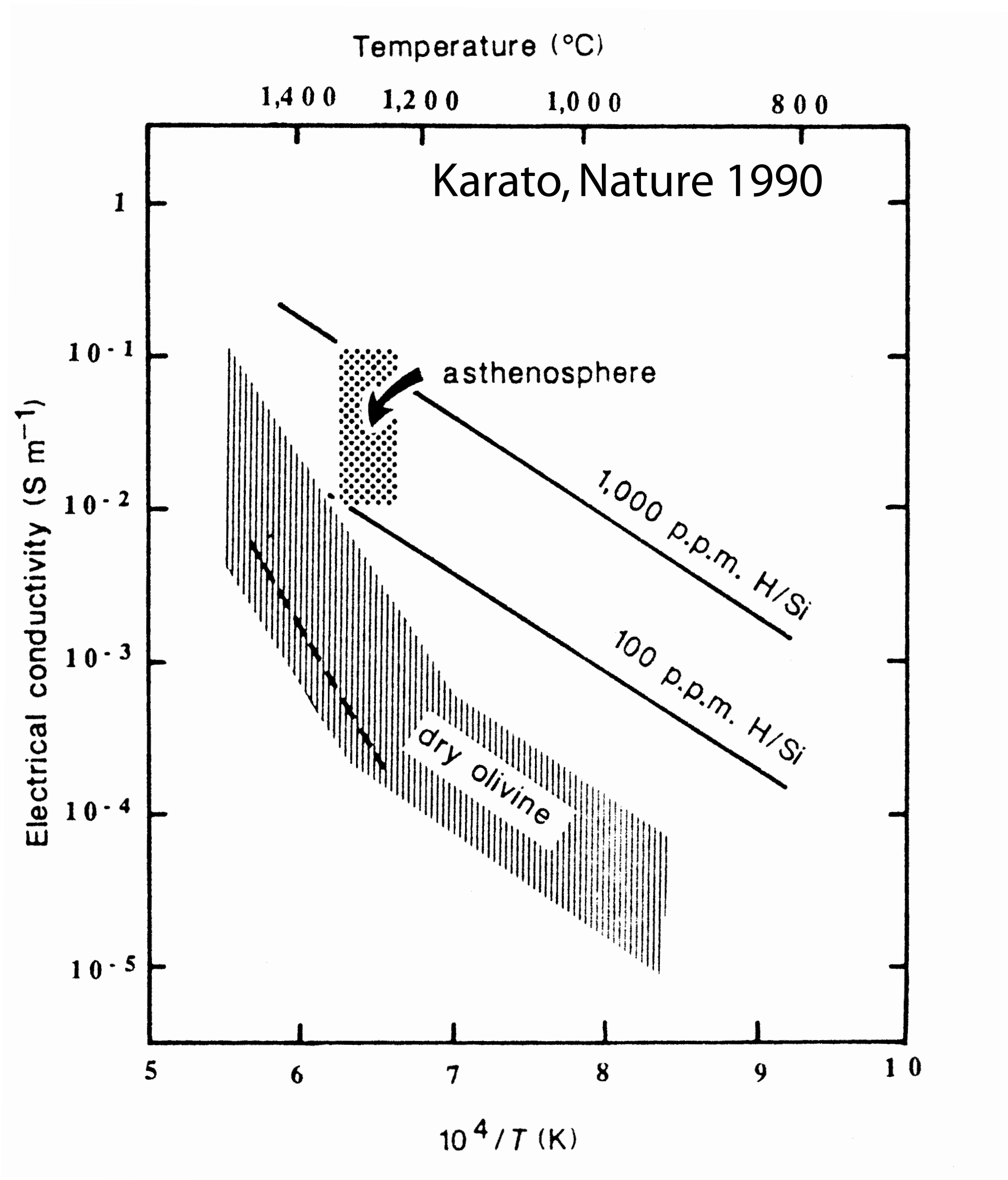


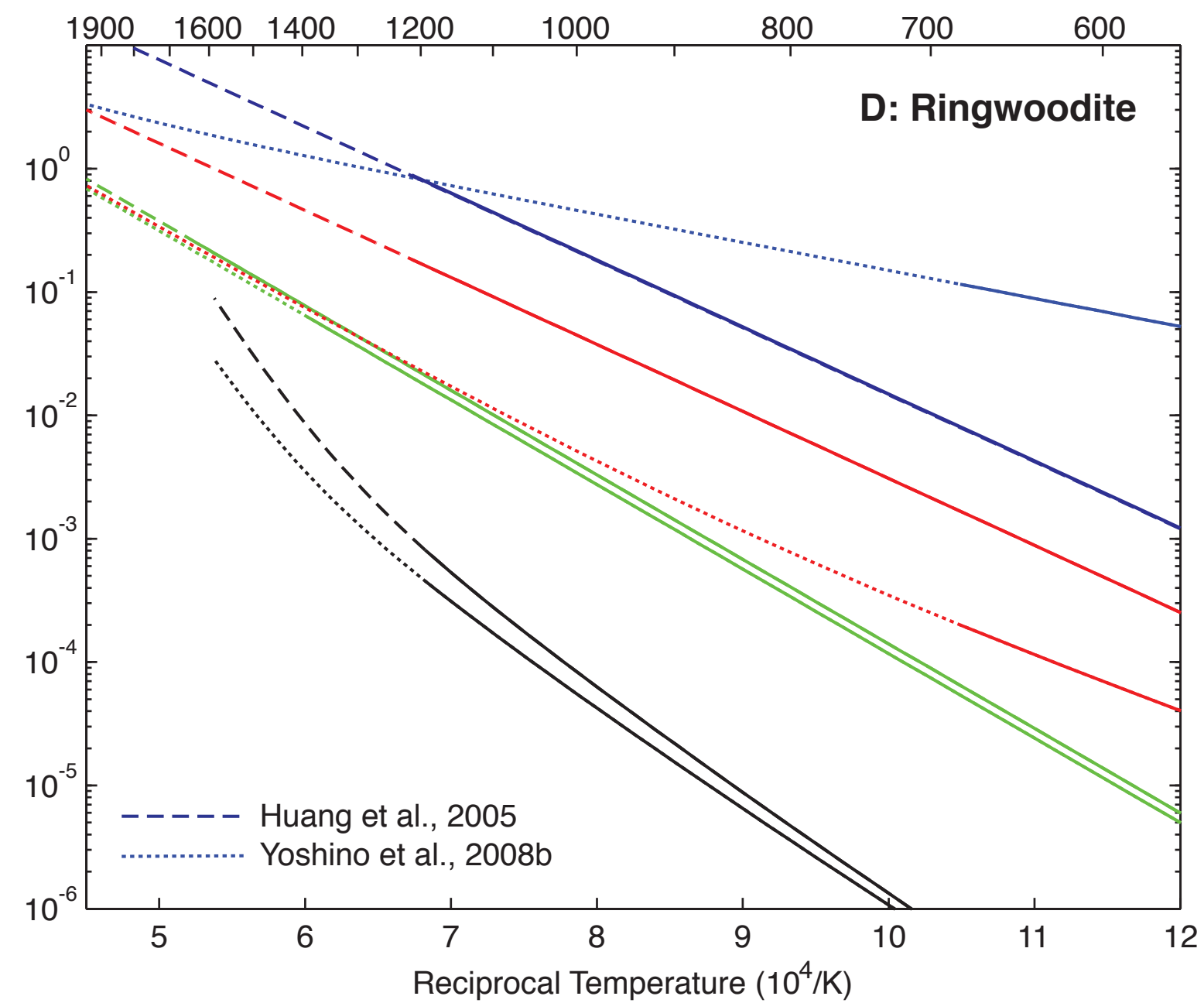
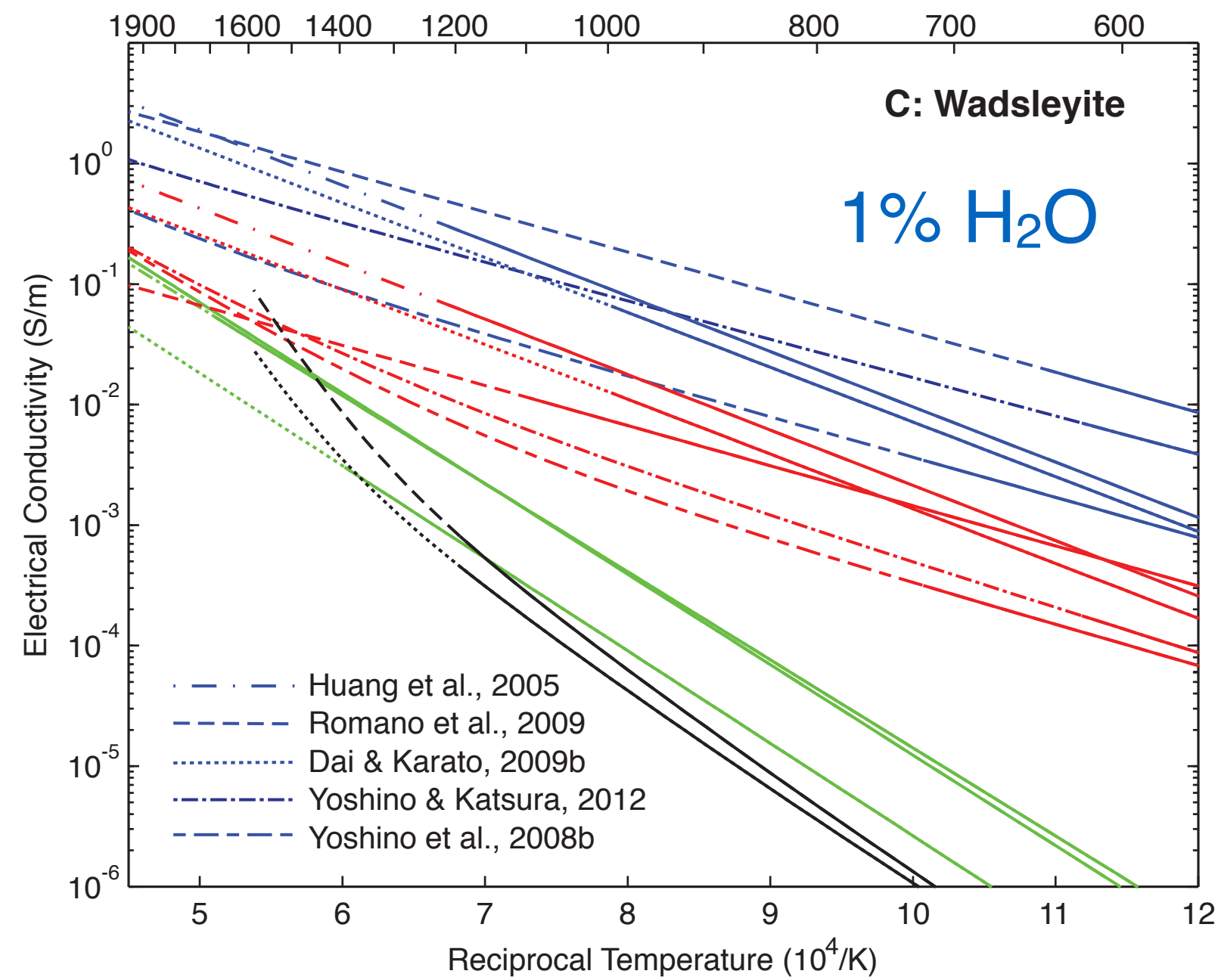
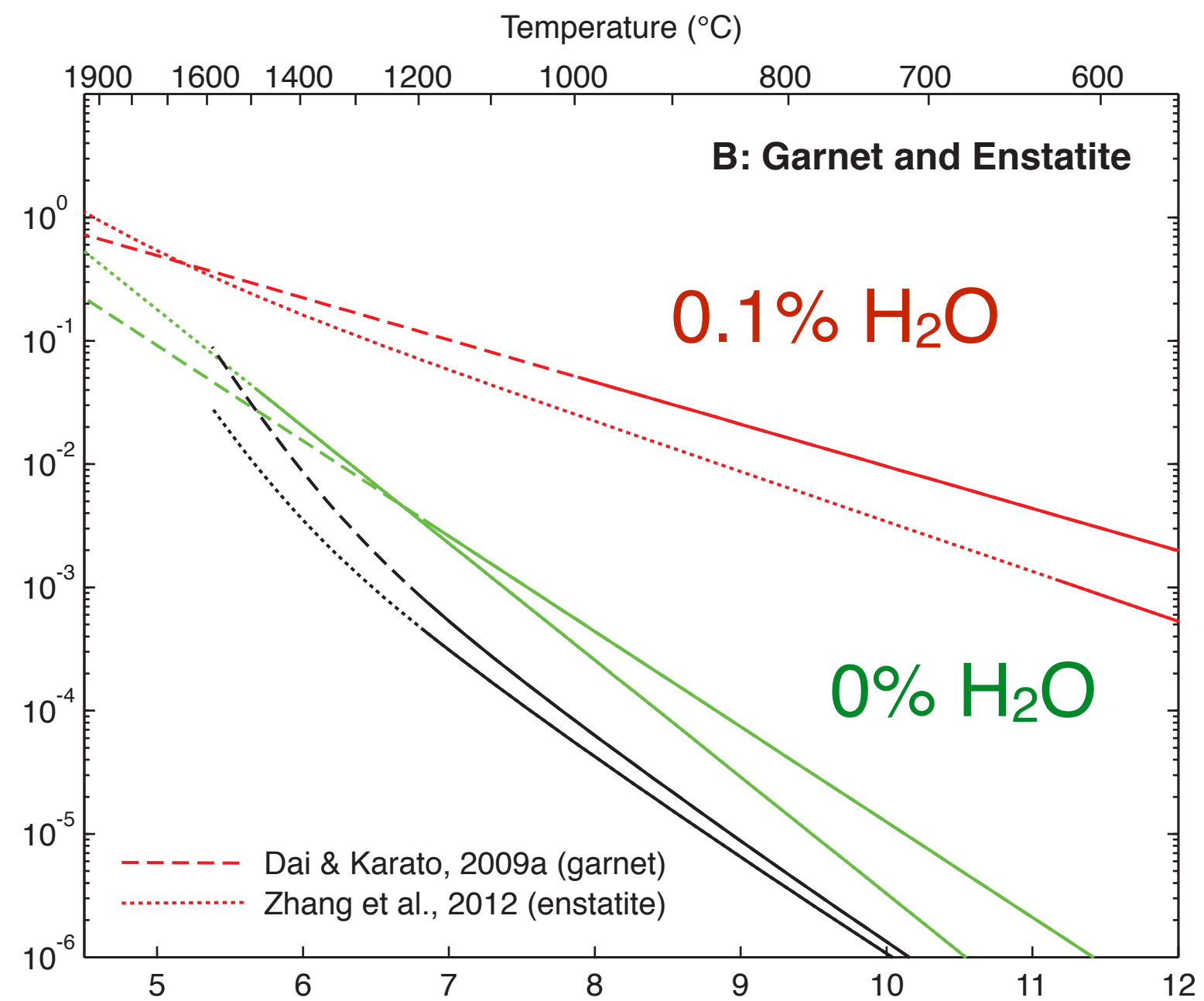
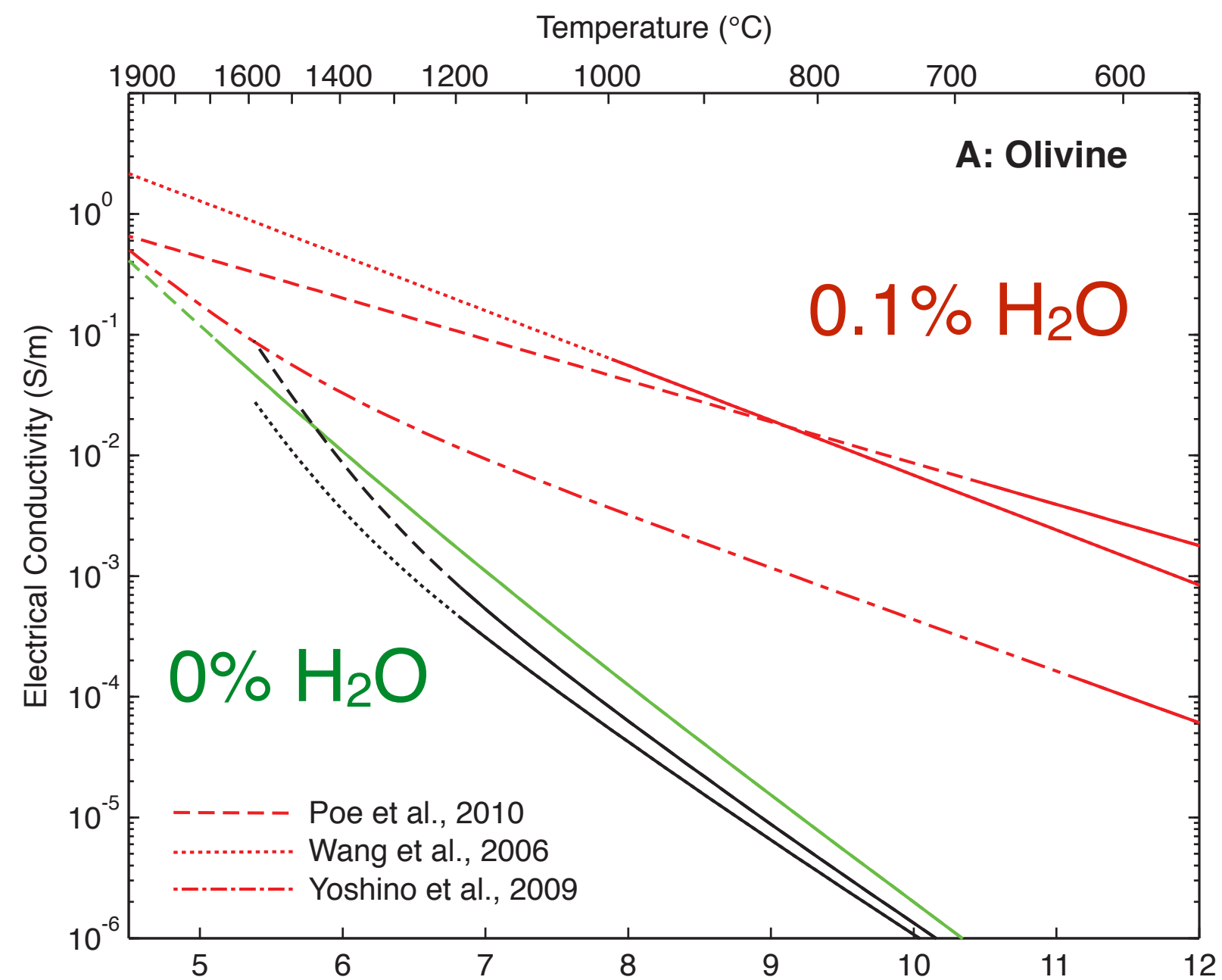


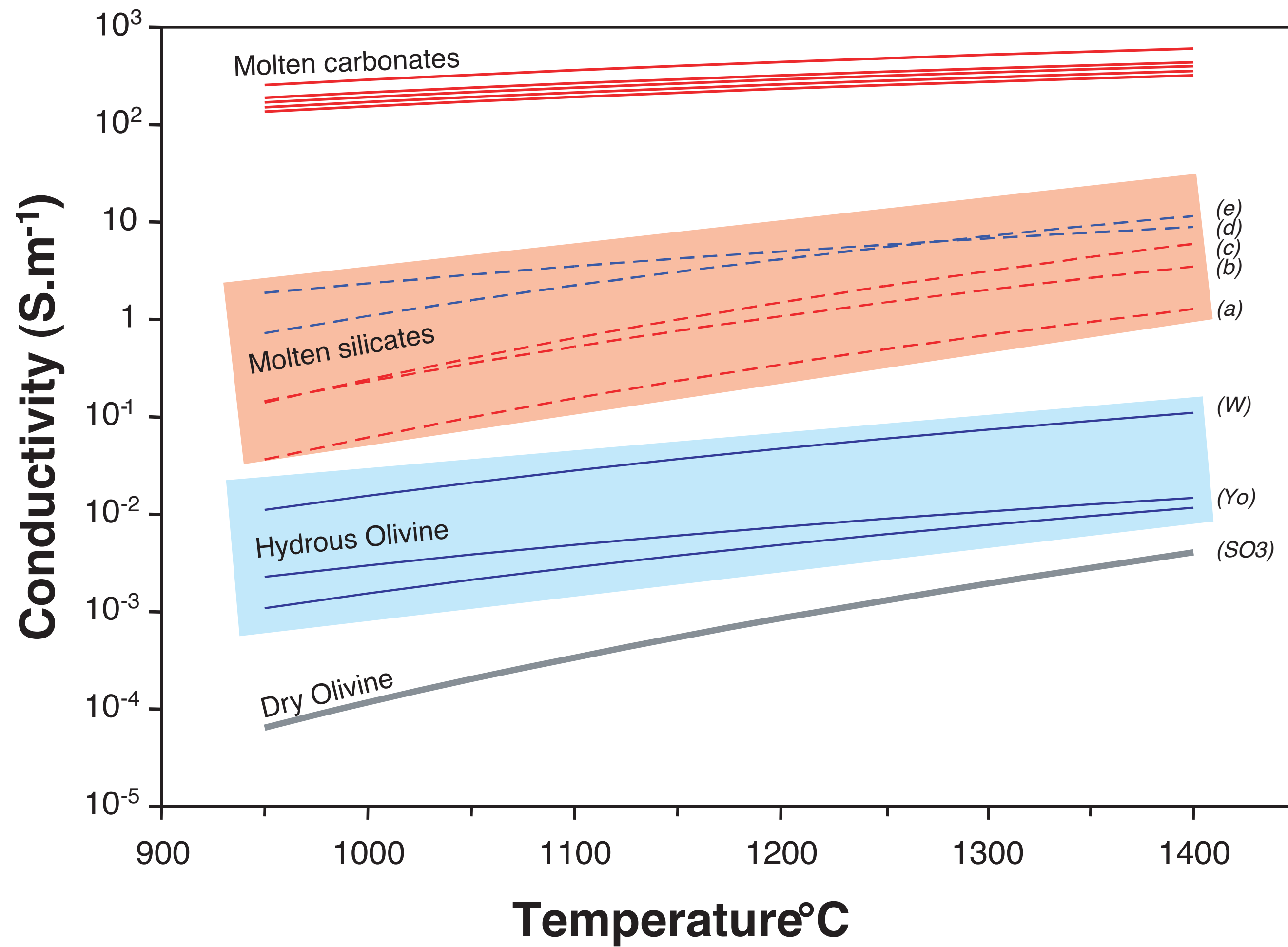
A wet mantle.



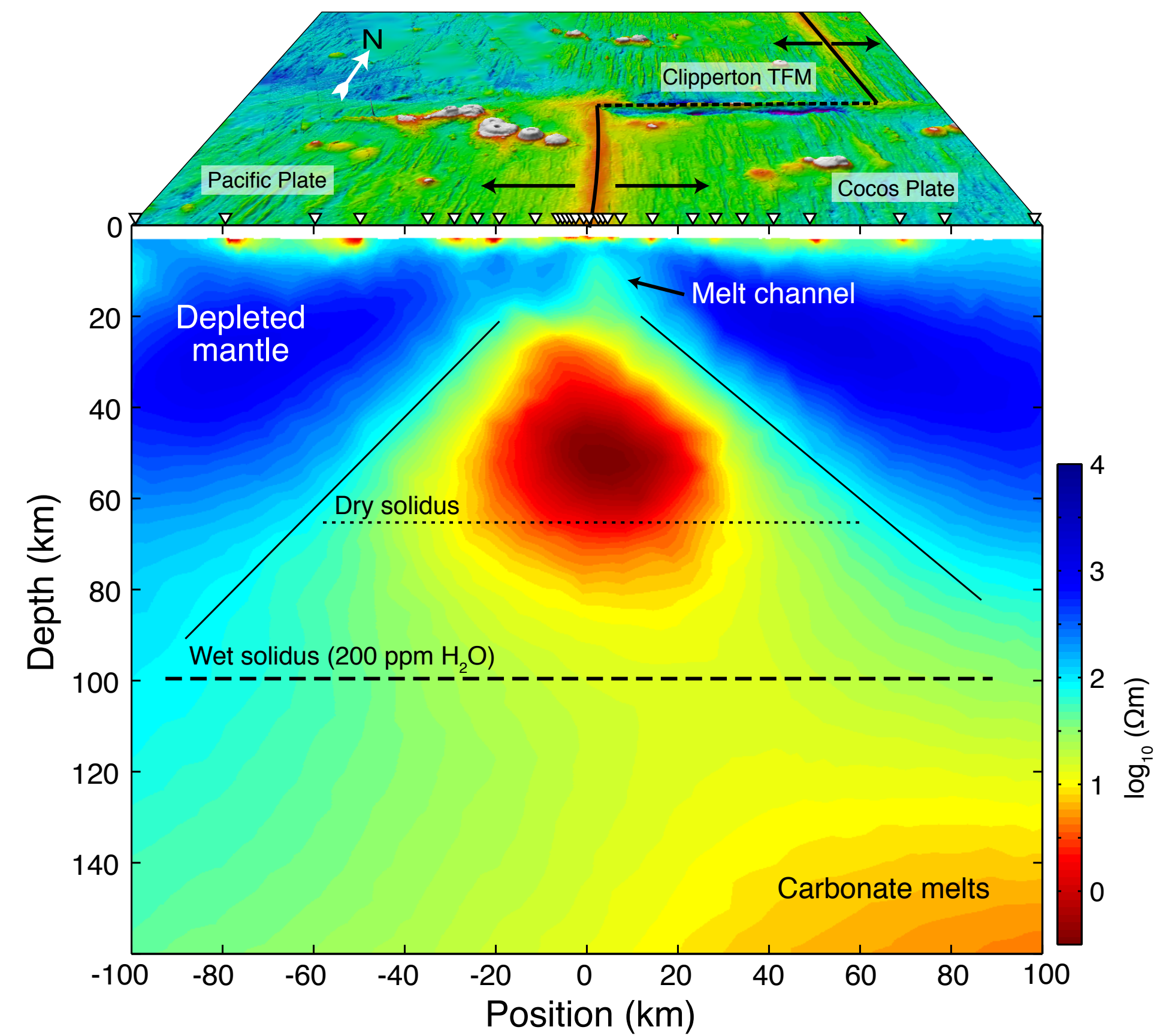






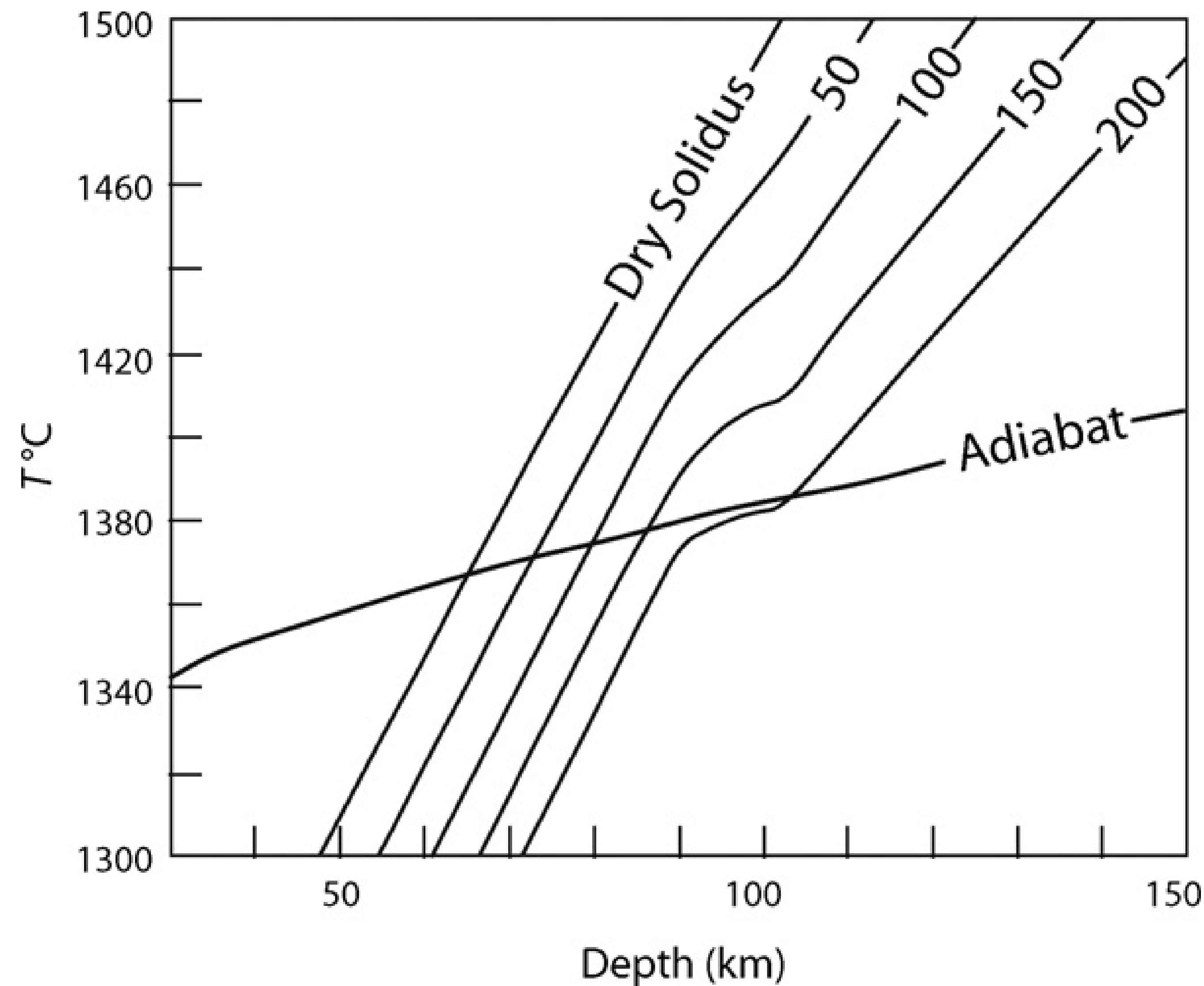


Gaillard et al. (2008)



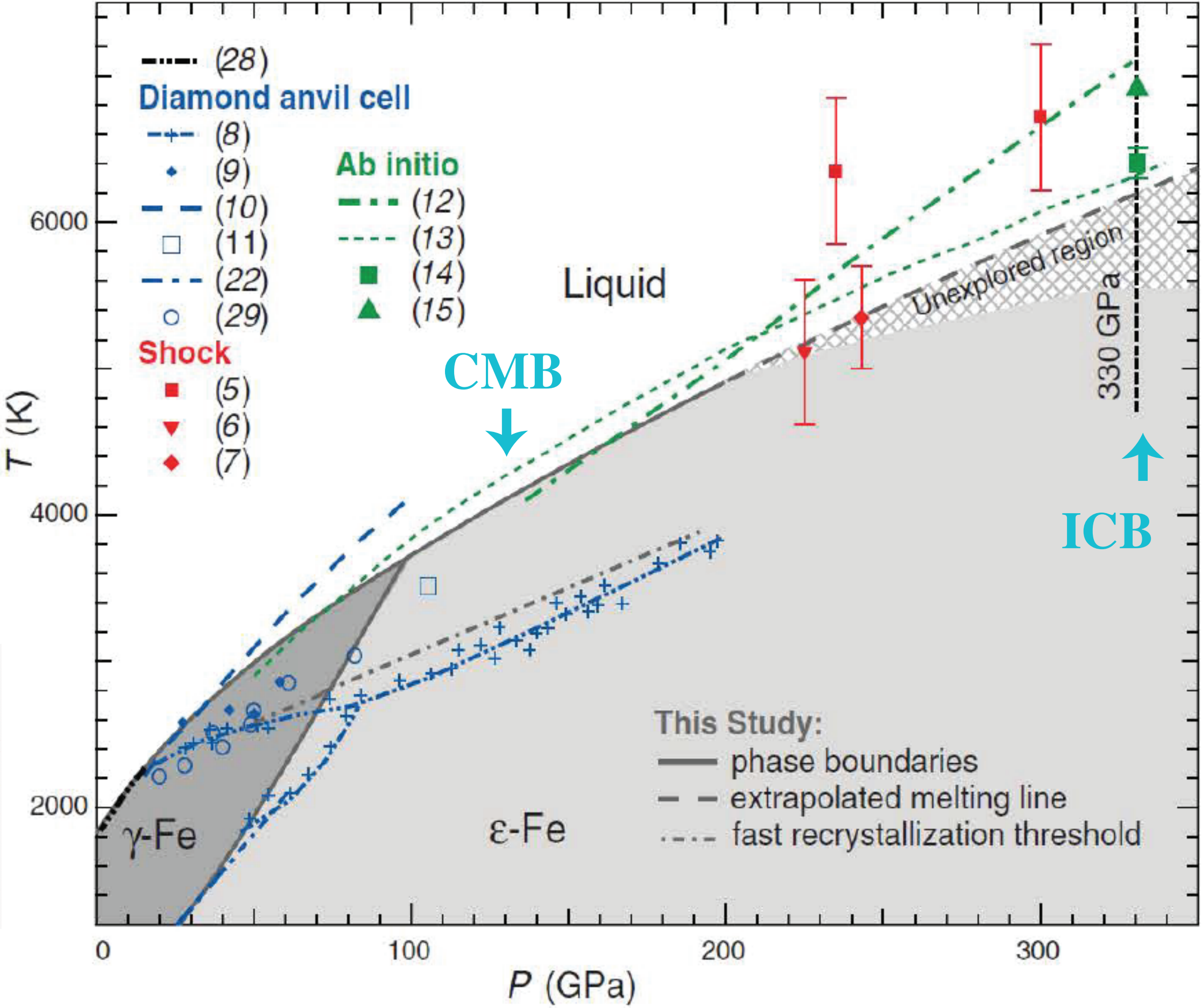
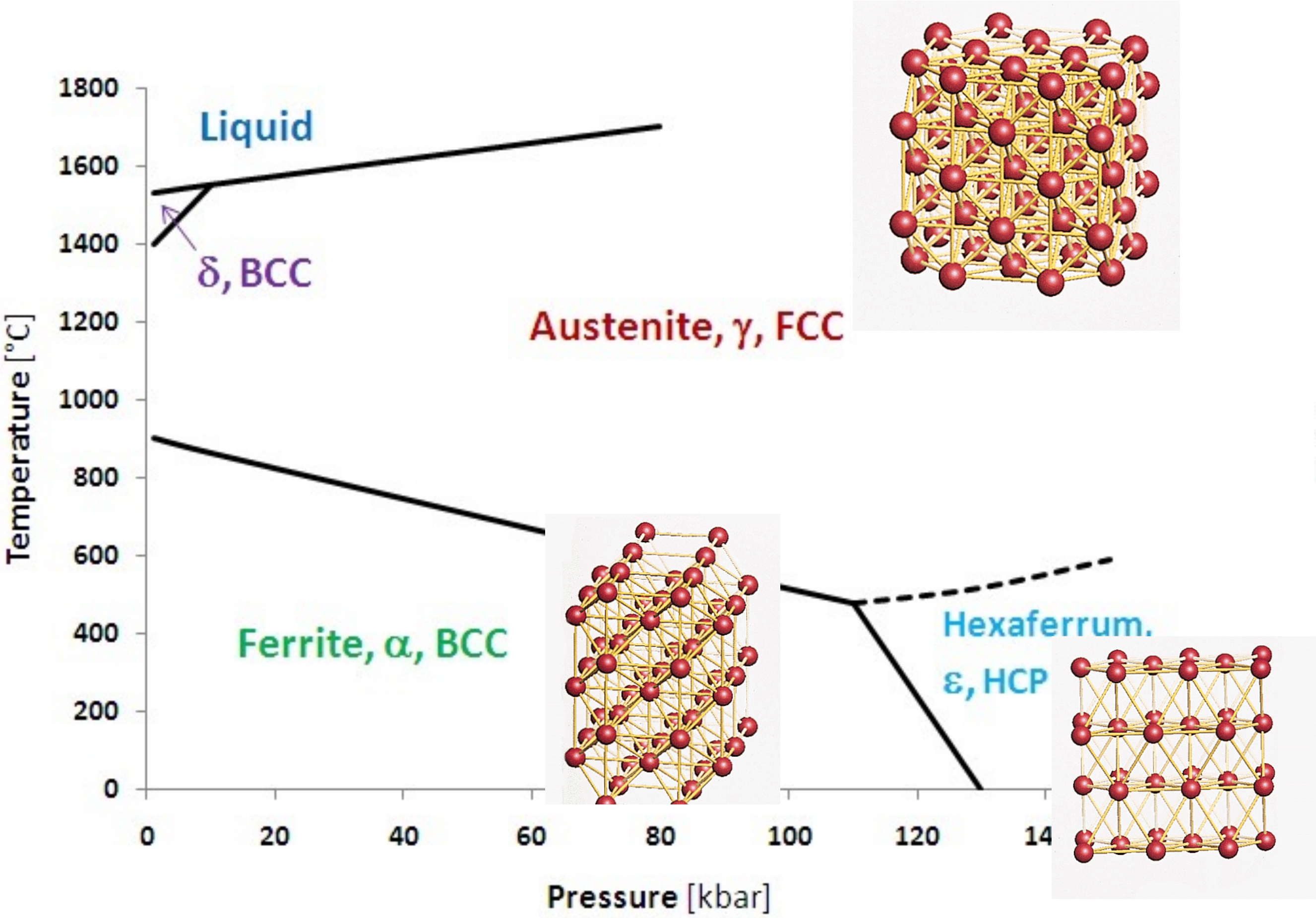
Key et al. (2013)

A few hundred parts per million water lowers mantle solidus by 100°C



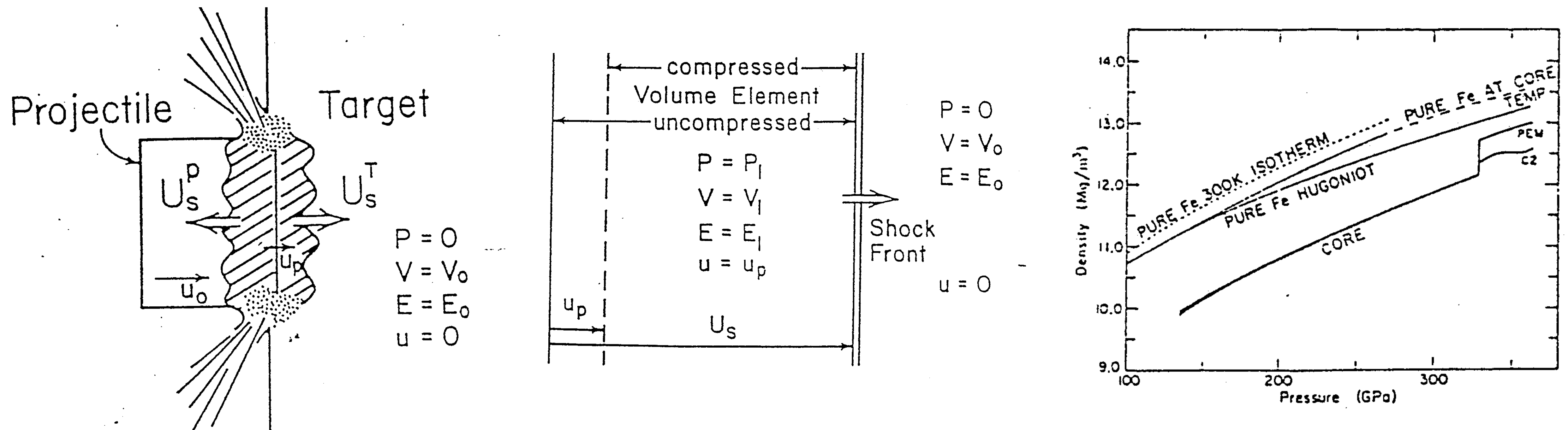
Hirschmann et al. (2008)

The core:



Shock wave experiments

Stacey and Anderson (2001, PEPI) estimated the resistivity of the outer core to be $2.1 \times 10^{-6} \Omega\text{m}$ and inner core $1.6 \times 10^{-6} \Omega\text{m}$, based on shock wave experiments of iron with Si and Ni impurities and the idea that for an “ideal” metal the conductivity is constant on the pressure-temperature melting curve (shock wave experiments showed that outer core density was lower than Fe).



However, more recent measurements using ab initio calculations and direct diamond anvil measurements put the outer core resistivity at $6\text{-}7 \times 10^{-7} \Omega\text{m}$, or three times the shock wave values.

