SIOG 231 GEOMAGNETISM AND ELECTROMAGNETISM

Lecture 18: Electrical Conductivity of Rocks, Crust, Mantle, and Core

Introduction

There are three basic conduction regimes for crustal, and mantle, rocks:

i) **Ionic conduction** of crustal rocks containing water. The mineral grains making up most rock-forming minerals are essentially insulators (e.g. quartz conductivity [resistivity] at surface temperatures is about 10^{-12} S/m [10^{12} Ω m]), and so the higher conductivity of water in pores and cracks determines the conductivity of the rock. Some examples:

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

In practice, I have found that quite drinkable stream water doesn't get more resistive than about 100 Ω m.

ii) Conduction dominated by minerals that are **good semiconductors**, such as graphite, magnetite, and pyrite, or **native metals**. These minerals may occur in trace amounts but may nevertheless form a well connected pathway, or in extreme cases they may account for the bulk of the rock (in the case of ore bodies).

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

iii) Thermally activated conduction by **point defects** in sub-solidus silicate minerals, or **electrolytic conduction** molten silicates, at elevated temperature in the deep mantle or crustal volcanic systems. In mineral crystals, point defect conduction is (simplified) associated with point charges that can move through the crystal either as a result of defects in the crystal structure or cations that can have mixed valency (e.g. iron).

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	

We will look at conduction in minerals during the next lecture. Here we will look at measuring conductivity and conduction in crustal rocks.

Laboratory Measurement of Conductivity

While the fundamental physical property of rocks and minerals is conductivity/resistivity, our laboratory equipment is designed to measure circuit resistance. Resistivity ρ and resistance R for a regular prism are related by

$$R = \rho L/A$$

where L is the length of the sample and A is the cross-sectional area of the electrode-covered faces. Resistance, of course, is given by $\Delta V/I$ where ΔV is the potential difference across the sample and I is the series current. From this it can be seen that if one takes a cubic meter of material (L = 1; A = 1), the series resistance in ohms across two opposite faces of the cube will be the same number as the resistivity in ohm-m.



A regular prism of material with resistivity ρ has a resistance R given by $R = \rho L/A$

Such a measurement can be made in practice on a regular prism (such as a rock core or mineral sample) when electric current is passed through the sample by means of two metal plates pressed to the end faces. This is called the *two-electrode method*, but because the potential drop across the current electrodes is measured along with the potential drop across the sample, it suffers from the limitation that the contact resistance of the electrodes must be much lower than the resistance of the sample. If L is small compared with A and the sample is of relatively high ρ this approximation is acceptable, because the contact resistance of the electrodes will be less than the resistance through the sample.

Otherwise, the solution is the *four electrode method* in which a separate pair of electrodes are used to measure potential drop. Now the potential drop across the current electrodes is not part of the voltage measuring circuit The solves the problem of contact resistance at the electrodes by measuring a potential difference across the center of the rock rather than the ends. Because modern voltmeters have very high input impedances, the potential electrode impedance simply adds to the already high input impedance of the voltmeter. The resistivity can be computed from $\rho = \Delta V. A/(I.s)$ where s is the potential electrode spacing.

Practical considerations often force the issue in favor of the two-electrode method (for example, measurements made on small samples at high temperature and pressure), but we will have seen that the four-electrode method is the basis of the resistivity sounding method.

We mentioned the various conduction mechanisms in rocks; metallic, semi-conduction, ionic conduction,



Two- and four-electrode methods of measuring rock resistivity, showing equivalent circuit elements. R_c is contact or electrode resistance; R_r is the rock or sample resistance.

electrolytic conduction, and conduction by point defects. For ionic, electrolytic, and point defect conduction, the charge carriers are charged ions that cannot flow into metallic electrodes. When two different types of conductors meet, and one attempts to pass electric current between them, there will be a *polarization* at the boundary. The classic example of this will be a metallic electrode making contact with the ground or a laboratory sample. Electrons flowing though the electrode circuit set up an electric field in the electrolyte. Ions drift through the fluid in response to this field until they encounter the electrodes, where they have to stop. The initial effect of this is to increase the impedance of the fluid (and change the phase of the conduction current) by depleting the ions available for transport and the distance over which they can migrate. The second effect is that the ions will then participate in reversible and irreversible electrochemical reactions with the electrodes.

Polarization at the sample-electrode interface is controlled by using an AC current, usually of around 1 kHz in laboratory studies, and around 1 Hz in DC resistivity methods. Since polarization creates a capacitive response, it is wise to measure the phase, as well as the magnitude, of the conduction current versus applied potential. A technique called *impedance spectroscopy* exploits this capacitive effect to examine the sample more closely, by varying the frequency of the applied voltage and monitoring both the in-phase (real) and out of phase (quadrature or imaginary) current. An impedance diagram is constructed, plotting imaginary versus real impedance for various frequencies (such a diagram is also called a Cole-Cole plot). An equivalent circuit of a resistor and capacitor in parallel will create a semi-circular arc on such a plot. If several conduction mechanisms are present, several arcs will be generated, and in particular, electrode contact impedance in two-electrode measurements will separate from the impedance of the sample. Grain surface impedance can also be separated from grain interior impedance this way (e.g. Tyburczy and Roberts, 1990: G.R.L. 17 p. 1985).

Binary Mixing Laws and Fluids

Rocks are often made up of two components, one very much more conductive than the other. For example, a gabbro could be mostly non-conducting silicate minerals with minor amounts of conductive magnetite. A sandstone can be non-conducting quartz saturated with water. A mantle rock can be sub-solidus silicates of several hundred Ω m with conductive melt between the grains. Rather than make measurements on every



Impedance spectroscopy. The top diagram shows an equivalent series circuit, and the lower diagram shows the ideal measurement that would be made on a rock sample. Frequency increases towards the origin.



Example of impedance spectroscopy on a real sample (from Roberts and Lin, Water Resources Res., **33** p 577).

possible combination, **binary mixing laws** can be used to predict the conductivity of the bulk rock as a function of the conductive fraction. Alternatively, and most important for the hydrocarbon industry, rock porosity can be estimated from resistivity measurements made in boreholes (well logs).

Let's look at the conductivity of a couple of fluids:

Aqueous electrolytic conduction is associated with ions dissociated in water, and is arguably the most important conduction mechanism in crustal rocks. Seawater has a concentration of dissolved salts of about 35 g/l. About 27 g/l is sodium chloride, but seawater also contains magnesium, sulfate, calcium, potassium, bicarbonate and bromine in significant quantities, as does groundwater.

Mobility increases with temperature because the viscosity of water decreases with temperature, and for seawater conductivity is approximately

$$\sigma = 3 + T/10 \quad \text{S/m}$$

for temperature T in Celsius. However, for water under pressure, this linear relationship breaks down at around 200°C, and saltwater conductivity peaks at between 300 and 400°C. The definitive work on this subject is by Quist and Marshall (1968) *J. phys. Chem.* **71** pp. 684-703. We can make an improved model for seawater conductivity by taking the cubic relationship of Perkin and Walker (JGR, vol 77, p 6618, 1972) which is accurate over the $0-25^{\circ}$ C range and decreasing their coefficient of the cubic term by only 15% to make the extrapolation match the 100–200°C data of Quist and Marshall (1968), yielding

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

(Constable et al., 2009, JGI, vol 176, p 431).

Clearly, water conductivity will depend on salinity as well as temperature. Indeed, one measure of salinity, the "practical salinity unit", or PSU, which is defined in terms of electrical conductivity. The relationship is mostly linear, as far as I can tell, but obscured by corrections for temperature and pressure (yes – this is all about CTD measurements). The conversion is enshrined in a UNESCO 1983 standard algorithm, the PSS-78 salinity. It is easy to find online calculators and computer code to do the conversion from conductivity to salinity and vice versa.

Magma conductivity is approximately that of seawater, and is associated with diffusion of ions in a highly polymerized structure. So, it is not surprising that again one observes a thermally activated Boltzmann type conductivity, which for tholeiitic melt above 10 kbar pressure is approximately

$$\sigma = 10^{5.332} e^{-1.533 eV/kT}$$

(Tyburczy and Waff, 1983, J.G.R. 88 p. 2413).

Binary mixing laws are mathematical models that predict the bulk conductivity of systems made up of two conductive materials. As one might imagine, the physical geometry of the conductive material very much determines now conductive the bulk rock ends up.

The classic binary mixing relationship is Archie's Law, which (in spite of the name), is an entirely empirical relationship developed to explain the conductivity of sedimentary rocks containing water:

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

 σ_f is the fluid, or water conductivity, and β is the fluid fraction. In the case of a saturated rock, β is the porosity, but it is easy enough to express fluid content in terms of saturation and porosity. Here we



Electrical conductivity of 0.1 molal NaCl solution as a function of temperature and pressure, from Quist and Marshall.

have included the conductivity of the solid, σ_s , a modification attributable to Hermance (1979) who wanted to consider the conductivity of minerals near their melting point for partially melted rocks, although for sediments this is usually taken to be zero. The exponent m can be derived experimentally from a suite of samples for a given rock type, but is usually taken to be 2 for sediments. A smaller m corresponds to more efficiently connected pore space. The term β^m is called the formation factor.

A model of fluid filled tubes might be a reasonable representation of well-connected melt in a volcanic system:

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

One can get as complicated as one wants. A model of spheroidal inclusions with aspect ratio α is given by H. Schmeling (PEPI, **43** p 123). This model is perhaps useful because there are models of seismic velocity for the same geometry:

$$\sigma = \frac{1}{3}(\sigma_1 + \sigma_2 + \sigma_3)$$

where

$$\sigma_i = \sigma_s \frac{(1-\beta)(n_i-1)\sigma_s + (n_i - (n_i - 1)(1-\beta))\sigma_f}{(n_i - 1 + \beta)\sigma_s + (1-\beta)\sigma_f}$$
$$n_1 = n_2 = \frac{-2h^3}{h - (1 + h^2)tan^{-1}h}$$
$$n_3 = \frac{-h^3}{(1 + h^2)(tan^{-1}h - h)}$$

$$n = \sqrt{\alpha^{-2} - 1}$$

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

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

where the conductive fraction is maximally isolated, say spheres of conductors in a resistive matrix.

$$HS^{+} = \sigma_{l} + (1 - \beta) \left(\frac{1}{\sigma_{s} - \sigma_{l}} + \frac{\beta}{3\sigma_{l}}\right)^{-1}$$

where the conductive fraction is maximally connected through the material.



Binary Mixing Laws - Examples

Binary mixing laws. Here Archie's Law uses an exponent of 2.

Modification of Archie's Law for Clay-bearing Sediments

In sediments that contain clay (shales), it is observed that Archie's Law breaks down for low salinity/conductivity pore fluids. This is because the surface charge and the double-layer of the clay minerals we discussed in self potential methods also increases the effective electrical conductivity of the fluid close to the surface of the clays.

The classic work in this area is by Waxman and Smits (1968). Their equation for the electrical conductivity of a shale is

$$\sigma = \frac{1}{F^*} (BQ_V + \sigma_w)$$

where F^* is a formation factor, analogous to the term in Archie's Law, and Q_V is the volume equivalent of the cation exchange capacity. The cation exchange capacity is a measure of the number of moles of



Conductivity σ of clay-bearing sandstone versus the conductivity of the water σ_w saturating the rock. (from Ruffet et al., 1995). Note the non-linear behavior for low σ_w .

electric charge that are bound to the clay surfaces, per unit mass. The units are centi-moles per kilogram $(\text{cmol}_c/\text{kg}, \text{equivalent to older units of me/100g or meq/100g})$. Cation exchange capacity can be measured in the laboratory by exchanging the bound cations with cations of another type from solution, and measuring either how much has been taken up, or how much has been released. It is relatively low for chlorite, illite, and kaolinite, but relatively high for smectite. Soil humus also has a high cation exchange capacity. The multiplier for Q_V is

$$B = [1 - ae^{-\sigma_w/\gamma}]\lambda_{Na}^e$$

where σ_w is the conductivity of the pore fluid and λ_{Na}^e is a measure of the conductance of the sodium cations associated with the cation exchange capacity of the clay. The factor *a* corrects for the fact that λ_{Na}^e depends on water conductivity somewhat

$$a = 1 - \frac{(\lambda_{Na}^e)_{\sigma_W = 0}}{\lambda_{Na}^e}$$

and γ is some sort of volumetric equivalent. This is all very complicated, but one can see that in the case where Q_V is small or zero, the equation reduces to Archie's Law. Revil and Glover (1998) re-cast the equation in a form with only a couple of empirical constants that can be calibrated against laboratory measurements.

Pressure effects on binary systems

Normally, when one measures the electrical conductivity of fluid-filled crustal rocks as a function of pressure, increasing pressure decreases pore volume, and so conductivity decreases. However, if the dominant conduction is by conductive minerals, such as graphite or magnetite, increasing pressure can press these minor minerals into better electrical contact, in which case conductivity will increase with pressure. This is an important diagnostic of conduction mechanism.

Moving an Electric Charge



Ranges of cation exchange capacity, courtesy Wikipedia.

Electrical conduction in a material is accomplished by a movement of charge, which in practice means the movement of electrons, holes (the absence of an electron), ions or ion vacancies. Materials may be classified on the basis of the nature of the charge carriers and the type of movement. Generally, conductivity in a material is given by

 $\sigma = nq\mu$

where q is the charge of the mobile species, n is the concentration of the charged species, and μ is the mobility, or drift velocity per applied electric field, |v/E|.

Conduction in native metals is by means of valence, or conduction, electrons which do not take part in crystal bonding and are loosely bound to atoms. The filled electron shells and nucleus form ion cores which occupy only 10%–20% of the crystal volume, while the conduction form a 'sea' between them. This form of conduction is very efficient, resulting in room temperature resistivities for metals of about $10^{-7} \Omega m$. The resistivity of metallic conductors decreases with temperature because of thermal agitation of the conduction electrons, which impedes their movement in response to an electric field and therefore lowers the drift velocity. Native metals are fairly rare in surface rocks, but iron is responsible for the high conductivity in the core.

Metallic conduction electrons have long mean free paths because they don't get deflected by the *periodic* arrangement of ion cores, and only rarely get scattered off other conduction electrons. For metals

$$v = -eE\tau/m$$

where τ is the mean free time between collisions and *m* is the mass of the electron. For metals *n* is of order $10^{28} - 10^{29}/\text{m}^3$. The mean free path $(v\tau)$ is of order 1 cm at 4 K, 10^{-8} m at room temperature. Thus conductivity from metals is thus given by

$$\sigma = \frac{ne^2\tau}{m}$$

which can be thought of as an acceleration under an electric field (e/m) of charge of density ne for a time period τ .

Note that here v is the drift velocity (of order 10^{-4} m/s – the Fermi velocity at room temperature is much higher, around 10^{6} m/s). We can get an idea of the drift velocity from

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



Electrical resistivity as a function of pressure for a suite of rocks from the German deep drilling project (KTB). In the upper diagram resistivity goes up (conductivity goes down) as the confining pressure reduces the pore space and water content of the rock. In the lower panel, increasing pressure decreases the resistivity of the rock, which are known to contain sulphide minerals and graphite (from Nover et al., 1995).

where J is current density and c is charge density. If you consider a current of 1 amp in a wire with cross-sectional area 10^{-6} m² then $J = 10^{-6}$ Am⁻². The charge on an electron is 1.6×10^{-19} C so our charge density is of order 10^{-10} Cm⁻³. Thus our drift velocity is of order 10^{-4} m/s.

Scattering (which determines mobility μ and mean free time τ) is by means of phonons (lattice vibrations) and impurities. Phonons go to zero at 0 K and are proportional to temperature above some threshold, so resistivity ρ

$$ho \propto T$$

(That threshold is the Debye temperature, below which quantization of energy causes some vibration modes to be 'frozen' out. It is between 100 and 400 K for most metals.)

Semiconduction is the result of behavior in between metallic conduction and conduction in insulators. It is typical of ionically bonded binary compounds, such as PbS, ZnS, MgO, etc. There are no free electrons, as such, in a semiconductor, but an applied electric field can supply enough energy to move electrons from the valence band, across the band gap E_g , into the conduction band at higher energy levels. As a result of these few electrons, and the holes they leave behind in the lower energy levels, moderate conductivities are achieved, between about 10^{-5} and 10^5 S/m. Sulphide minerals are semiconductors with quite low resistivities.

For semiconductors,

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

where n and p are the carrier densities of electrons and holes (typically around $10^{19} - 10^{23}$ /m³), and μ_e, μ_h are the respective mobilities.

Carrier concentration is thermally activated and is

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

where k is Boltzmann's constant $(1.380 \times 10^{-23} \text{ J/K} \text{ or } 8.617 \times 10^{-5} \text{ eV/K})$. E_g is the activation energy, and has units of kJ/mol or eV, depending on the choice of k. Mobility is also only proportional to T, so the exponential term dominates. Such thermally activated processes are often termed Arrhenius relationships, and produce linear plots when $\log(\sigma)$ is plotted against 1/T.

Charge carriers can also be generated by impurities or doping; a divalent cation substituting on a trivalent site will have an excess electron which is available for the conduction band. These two conduction regimes, one determined by statistical mechanics and one determined by crystal impurities, is typical of solid state conduction. The first, purely thermally activated, variation in conductivity is the same for a given material and temperature, and is called *intrinsic* conduction. The second regime, which also has some temperature dependence but will vary from sample to sample with the amount of impurity, is called *extrinsic* conduction. In the intrinsic regime, holes must equal electrons because elevation of every electron into the conduction band will leave behind a hole. Impurities, however, can donate either holes or electrons to conduction.

Point defect conduction (also called solid electrolytic or ionic conduction) dominates when the band gap is too large for semiconduction, and is the result of moving ions and ion vacancies through a crystal structure. It is very difficult to move ionically bonded ions through a crystal lattice, so the resistivities of silicate minerals are very high; quartz has resistivities between 10^{10} and $10^{14} \Omega m$. Rock salt has a resistivity of $10^{12} \Omega m$ or so. It would, in fact, be close to impossible to move ions through a perfect lattice, but defects in the lattice allow the motion of ions and vacancies. Schottky defects are lattice vacancies and Frenkel defects are ions in interstitial positions. Impurities also constitute defects in the lattice, both in themselves and because they can promote vacancies to maintain charge balance. These are called *point defects*, compared with dislocations, line and plane defects, which tend not to contribute substantially to conduction.

Schottky and Frenkel defects are thermally induced, so the number of defects, and hence conductivity, increases with increasing temperature:

 $n_s = Ne^{-E_v/kT}$ (Schottky defects or vacancies) $n_f = (NN')^{1/2}e^{-E_i/2kT}$ (Frenkel defects or interstitials)



Figure 1 Extrinsic and intrinsic regimes in semiconductors. Extrinsic conduction occurs at lower temperature and is a result of electrons or holes generated by impurities (or doping). Intrinsic conduction is a result only of thermally activated charge carries associated with the pure crystal.



Figure 2 Defects in crystals.

where N is the total number of atoms and N' is the total number of interstitial sites. Again, however, defects can be generated by impurities. Thus a divalent cation on a monovalent site induces a cation vacancy to maintain charge neutrality.

The mobility of point defects can be related to diffusion, the flux J_N of atoms crossing unit area in unit time under the influence of a concentration gradient ∇N . The **diffusivity** or **diffusion constant** D is defined by **Fick's law**:

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

Diffusivities are found to vary with temperature, again, as a thermally activated Boltzmann process:

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

where E_d is another activation energy for diffusivity.

Mobilities are related to diffusivities by the Nernst-Einstein equation:

$$kT\mu = qL$$

so $\mu = qD/kT$ and the conductivity of, for example, Schottky defects becomes:

$$\sigma = n_s q \mu$$
$$= N e^{-E_v/kT} . q.qD/kT$$
$$= N q^2 D_o/kT e^{-E_v/kT} e^{-E_d/kT}$$

The exponential terms dominate, and so to a first approximatation conductivity is given by

$$\sigma = \sigma_0 e^{-E/kT}$$

where E is an apparent activation energy associated both with defect concentration and mobility. (Much of the above material can be found in Kittel (1986) *Introduction to Solid State Physics, 6th ed.* by Wiley.)

It should be noted at this point that strictly speaking, the diffusivity in the Nernst-Einstein equation is the self-diffusion coefficient, defined as the diffusivity when the concentration gradient equals zero. It is related to the diffusivity by

$$D^* = D\frac{\partial \ln c}{\partial \ln a}$$

where a is the thermodynamic activity of the charge carrier and c is its concentration. It accounts for interactions between the charged species. Diffusivity is measured by creating a chemical gradient in the crystal, and self diffusion by isotopic tracers.

Often as not there are several point defects in the mineral (olivine, for example, has about 7 that have been studied to varying degrees). Figure 3 presents a model of 11 different charge-carrying defects in silicate perovskite, and olivine would have a similar suite of defects. Description of the defects is handled by the Kröger-Vink notation, in which the main character is the actual species involved (a 'V' denotes a vacancy), the subscript is the crystal site for a normal lattice (in interstitial site is denoted by 'I'), and the superscript is negative, positive, or neutral charge shown as ', •, or x respectively. Thus Fe_{Mg}^{\bullet} is a Fe^{3+} ion occupying a Mg^{2+} site resulting in a net charge for the defect of +*e*. Notice that in Figure 3 the concentration of defects depends on the oxygen activity. We will talk more about that later.

In spite of the variety in defect types, the dominance of the exponential term in the expression for conductivity means that at a given temperature one mechanism is likely to dominate over another. As temperature changes, different activation energies will cause the dominant conduction mechanism to change, so conductivity if often expressed as

$$\sigma = \sum_{i} \sigma_{i} e^{-E_{i}/kT}$$

.

This Boltzmann relationship between temperature and conductivity can be linearized by taking log σ as a function of 1/T, to form an Arrhenius plot. For a single conduction mechanism, data plotted in this way will be a straight line. For mixed conduction, a number of lines may be observed as a function of temperature. Figure 4 shows an example of two conductivity mechanisms being expressed as a sample is heated from 500°C to 1,200°C.



Figure 3 A defect model for silicate perovskite, showing concentrations of various defects as a function of oxygen activity (f_{O_2}) (from Hirsch and Shankland, 1991, GRL **18** p 1305).

Pressure can also have an effect on conductivity, which may be modeled as

$$\sigma = \sigma_0 e^{-(E + P\Delta V)/kT}$$

where P is pressure and ΔV is called the activation volume. Pressure usually has a minor effect compared with temperature, unless it changes the mineral phase and causes a more mobile or numerous defect to dominate.

Defects undergo chemical reactions that maintain charge balance and species, but that can create and destroy charge-carrying defects. For example

$$Fe_{Mg}^{x} \rightleftharpoons Fe_{Mg}^{\bullet} + e'$$

This represents the creation of a ferric (+++) ion sitting on a magnesium site in the crystal lattice, and a free electron, from a ferrous (++) ion sitting on a magnesium site. Because the magnesium site is normally occupied by a (++) Mg ion, the ferrous interloper, while a crystal defect, is not a charged defect. However, the ferric ion has a net charge of (+) for this crystal site, and of course the free electron has a negative charge.

We shall discuss this in more detail later, but the biggest effect on defect chemistry is oxygen. Oxidation and reduction is associated with an exchange of charge, so oxidation state changes the number of charged defects in a mineral. Figure 3 shows a model for perovskite that gives you some idea of the potential for charged defects in a mantle mineral.



Figure 4 Electrical conductivity of cobalt olivine (Co_2SiO_4). The two lower curves are data collected on initial heating; the upper curve represents measurements made at a slightly different oxygen activity (dealt with later in the course). From Hirsch, 1990, Phys. Chem. Min. bf 17, p 187.

Maintaining the Chemical Environment

When measurements are made at high temperature, to predict the behaviour in the deep Earth and to establish an activation energy for the conducting species, care must be taken to control the chemical environment of the sample so that it is not altered during measurement and that the measurements are applicable to the natural environment of the sample. The most obvious problem is oxidation during heating; even laboratory grade inert gases have enough contaminant oxygen to place some minerals outside their stability fields. Figure 9 shows the stability fields of olivine.

For low pressure experiments, a controlled mixture of $CO:CO_2$ or $H:CO_2$ is passed over the sample. For a given temperature and gas mix ratio, there is a known equilibrium concentration of oxygen developed; any excess is consumed by the reducing agent (CO or H), and any deficiency is liberated by the oxidizing agent (CO₂). For example

$$2CO + O_2 \rightleftharpoons 2CO_2$$

so even if the starting gasses contained contaminant oxygen, it will be consumed until only the equilibrium amount remains. This approach is limited on the reducing side by the carbon stability field, where carbon precipitates from the gas mix onto the sample (not good for conductivity measurements!).



Figure 9 Stability fields of olivine versus temperature and oxygen fugacity. M = magnetite, H = hematite, O=olivine, S = silicon, W = wüstite, I = iron. Gas mix ratios are indicated as CO₂:CO. The shaded area is the region where olivine is stable.

The usual mistake, often made in early studies in which inert gas mixes such as argon were used, is to oxidize the olivine to hematite. No gas is pure enough; at 700°C one can see that olivine oxidizes above about 10^{-8} Pa O₂, or one part in 10^{13} oxygen. 99.999 percent reagent gases may have up to 1 part in 10^{6} , or 0.1 Pa, O₂. A more interesting mistake is to reduce the sample to iron (Figure 10). The important thing to note is that once iron is removed from olivine, it is stable throughout the olivine stability field as a conductive phase, and will never return to the olivine in these experiments.

Such control on the sample environment is called a chemical *buffer*. In this case the partial pressure of oxygen is being controlled, which is often termed oxygen fugacity or f_{O_2} . We have already seen that f_{O_2} control is not only important to keep the sample within its stability field, but can also determine the concentration of defects within the crystal (or polycrystal). For high pressure measurements, gas buffers can't be used. Instead, mixes of solid chemicals are used. Other problems associated with the chemical state of the sample are iron loss to platinum electrodes, and migration of ions such as silicon between constituents of the sample.

Since the two-electrode method is usually used for relatively resistive samples, and often at high pressure, care has to be taken to ensure that the dominant conduction path is through the sample, and not through the sample holder and surrounding apparatus. Figure 11 shows an example of a furnace designed to control the oxygen activity surrounding the sample and to minimize conduction leakage around the sample. The electrodes in contact with the sample are made of iridium, rather than platinum, to minimize iron



Figure 10 Iron precipitation from olivine under reducing conditions (from Boland and Duba, JGR, 91 p 4711)

loss. The thermocouple leads, which allow the temperature to be measured on both sides of the sample (important for thermopower measurements), also serve as electrode leads for a 2-electrode measurement. For thermopower measurements, the entire assembly can be moved up or down in the furnace/cooling system to create a temperature gradient across the sample.

0.1 High pressure measurements

The surface pressure gas mixing furnace is unsurpassed in terms of making measurements under finely controlled f_{O_2} , but if one wishes to examine electrical conductivity of lower mantle phases (minerals), these need to be either made within a high pressure apparatus and bought back to surface pressures for measurement, or measured under pressure. The latter is clearly preferably if one wishes to study the minerals under conditions representative of the lower mantle, and/or to measure and activation volume.

There are three basic types of high pressure apparatus. The first is the *piston and cylinder* apparatus, which is exactly what it says and is suitable only for relatively low pressures, although it does have the advantage that gas mixes could be used to control f_{O_2} . The second is the multi-anvil cell (Figure 6), which uses a set of carefully shaped steel, tungsten carbide, and/or sintered diamond anvils to turn the force of a 1000+ ton uniaxial press into a triaxail confining pressure of up to several tens of GPa (40 GPa is about 1000 km deep). Figure 23 shows a sample capsule used for conductivity measurements of high pressure olivine phases in a multi-anvil cell.

Finally, the diamond anvil cell allows similar or greater pressures to the multi-anvil cell with a much smaller experimental setup and the possibility of optical interaction with the specimen. X-ray experiments can be made through the diamond, and lasers used to locally heat the sample. However, the need for a gasket as part of the sample confinement makes electrical conductivity measurements difficult.

0.2 Thermopower Measurements

In a gas-mixing furnace such as shown in Figure 11 of the last lecture, the assembly can be moved up or down



Figure 11 Gas mixing furnace for making electrical conductivity measurements at room pressure and high temperature (after Duba et al., AGU Mono. 56, p 207). The mixture of CO and CO_2 is controlled by separate mass flow controllers for each gas. The vertical size is about 60 cm.



Figure 6 High pressure conductivity cell for use in a multi-anvil press. From Xu et al., 1998, Science, **280** p 1415.



Figure 7 A diamond-anvil setup designed to measure precise strains using an optical technique (from Meade and Jeanloz, in High Pressure Research in Mineral Physics, AGU, 1987, p 41). The size of the sample area is less than 1 mm in diameter.

to produce a temperature gradient across the sample that can be measured using the two thermocouples. The resulting thermoelectric effect, also known as the Seebeck effect, can be measured as an EMF between the two electrode wires. The thermopower Q is defined as

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

Figure 8 illustrates the concept behind the thermoelectric effect. Mobility of defects is less on the cold side of the sample, and so an excess 'condenses' there. For a charge carrying defect, this results in an electric field across the sample that can be measured with a suitable high-impedance voltmeter. The sign convention for Q is such that the sign of the thermopower agrees with charge-carrying defect. Thermoelectric power is inversely proportional to the concentration of charge carriers, and is equivalent to the entropy per charge carrier. Expressions for this are of the form:

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

Tuller and Nowick (1977, J. Phys. Chem. Solids **38** p 859). Here *c* is the fraction of sites which contain a charge carrier, *q* is the charge of the defect, β is a degeneracy factor (for electrons β is usually taken to be

equal to 2 to account for the two possible spin states), S is the vibrational entropy associated with the ions (usually considered negligible) and k is Boltzmann's constant. Thus for polaron hopping

$$Q_{Fe} = \frac{k}{e} \ln 2 \frac{(1 - [Fe_{Mg}^{\bullet}]/[Fe_{Mg}^{\times}])}{[Fe_{Mg}^{\bullet}]/[Fe_{Mg}^{\times}]}$$

and for magnesium vacancies

$$Q_{Mg} = -\frac{k}{e} \ln \frac{(1 - [V_{Mg}^{''}]/[Mg_{Mg}^{\times}])}{[V_{Mg}^{''}]/[Mg_{Mg}^{\times}]}$$

For an electronic semiconductor, thermoelectric power is given by

$$Q_e = -\frac{k}{e} \left(\frac{E_c - \mu}{kT} + \frac{3}{2} \right) \tag{1}$$

(Kittel, 1986, Introduction to Solid State Physics, 6th ed. p212) where $E_c - \mu$ is the difference between the conduction band energy and the chemical potential (sometimes called the Fermi level).



Figure 8 Concept diagram for the thermoelectric effect. Charge carrying defects 'condense' on the cold side of the sample, creating an electric field that can be measured across the electrodes.

For mixed conduction with contributions from various defects, total thermoelectric power is given by the thermopowers of the individual charge carriers weighted by the contribution to the total conductivity (Hannay, 1959, Semiconductors, p375), for example

$$Q = Q_1 \frac{\sigma_1}{\sigma} + Q_2 \frac{\sigma_2}{\sigma} + Q_3 \frac{\sigma_3}{\sigma}$$

where σ_1, σ_2 and σ_3 are the contributions to conductivity from various defects and σ is the total conductivity.

Because thermopower is dependent only on concentration, and not on mobility, it provides an important tool for the study of charge transport in minerals.

Anisotropy

So far we have only considered the case in which conductivity is isotropic. In general conductivity may depend on direction.

As with porosity, the nature of anisotropy depends on scale, which can loosely be classified as crystallographic anisotropy, textural anisotropy, and structural anisotropy as the scale length gets progressively larger. Generally we can consider just three orthogonal axes:

$$\sigma = \begin{pmatrix} \sigma_x & & \\ & \sigma_y & \\ & & \sigma_z \end{pmatrix}$$

where most for structural anisotropy commonly x, y, z correspond to two horizontal and the vertical direction, although any general case can be rotated into three principal axes.

Crystallographic anisotropy is associated with variations in conductivity of the mineral itself. The principal components of crystallographic properties must lie along the crystal axes, and so it is sufficient to measure and specify conductivity along these directions. As an example, olivine, an orthorhombic mineral dominant in the upper mantle, is mildly anisotropic. Figure 14 shows measurements of olivine anisotropy, made on olivine derived from mantle xenoliths found in San Carlos indian reservation, Arizona. The [001], or c-axis, is most conductive, but still barely more than a factor of 2 greater than the other axes. The [100] and [010] (a- and c-axes) are of similar, with the a-axis of intermediate conductivity. Clearly, crystal anisotropy won't produce an effect that is observable in the field unless there is a preferential crystal orientation in the rock. Seismic and deformational models of the upper mantle suggest that the olivine a-axis will be aligned in the direction of plate motion, but since this axis is of intermediate conductivity, this won't produce an observable signal. If hydrogen conduction is important, anisotropies between the a and b axes could be up to 100, but there is still a lot of uncertainty in the laboratory measurements of hydrated olivine. We will revisit this issue when we discuss the possibility of hydrogen conduction in olivine.

Textural anisotropy is associated with the fabric of the rock. A common example of this type of anisotropy is found in sedimentary rocks that have well developed bedding, either as a consequence of platy or tabular mineral grains that preferentially fall flat during deposition, or by fine scale interbedding. In this case conductivity will always be higher in what were originally the sub-horizontal directions (i.e. foliation direction), and lower in the direction across the beds. *Anisotropy ratios* (σ_y/σ_z) of up to 2-10 are possible in this way.

Structural anisotropy is caused by macroscopic features that would normally be resolved by geological mapping but that are too small in relation to the electrical measurements to be resolved. For example, interbedded, meter-thick sedimentary horizons of different resistivity that are buried 10 - 100 m deep will appear anisotropic to a surface-based electrical method but not to borehole logging.

In principle all three principal directions of conductivity can vary – triaxial anisotropy. This is quite often the case for the conductivity of single crystal minerals, which we shall look at later. When crustal rocks are anisotropic it is usually uniaxial anisotropy– that is only one of the three directions differing from the other



Figure 14. Data (symbols) and model fits (lines) for electrical conductivity of San Carlos Olivine along the three crystallographic axes as a function of f_{O_2} at a temperature of 1,200°C (data from Du Frane *et al.*, 2005). Anisotropy is not strong, and the crystal axis most likely to be aligned in the mantle, [100], is of intermediate conductivity.



Relationship between geological and mathematical descriptions of anisotropy.

two. It is interesting to consider the relationship between the mathematical description and the physical interpretation of the 6 possibilities associated with uniaxial anisotropy (Everett and Constable, 1999).

Note that for well-connected conductors in an anisotropic material, the conductivity in the direction of the aligned conductors can exceed the HS upper bound.

Conductivity of Mantle Minerals

The Mantle

Before we can discuss mantle conductivity, we need to remind ourselves of the composition and temperature of Earth's mantle. Figure 10 shows a model of mantle mineralogy in pictorial form.



Figure 10. Mantle mineralogy, after Ito and Takahashi (1987: AGU Mono. 39, p. 221). Gar = garnet, Opx and Cpx are ortho- and clinopyroxene, Mw = magnesiowüstite, St = stishovite, Ca-P and Al-P are CaO and Al₂O₃ rich phases, respectively.

Olivine is the major component of the upper mantle. It is an orthorhombic magnesium-iron silicate, $(Mg_{1-x}Fe_x)_2SiO_4$ where x is typically 0.1 in the mantle. The magnesium and iron end-members are called forsterite and fayalite, respectively.

Wadsleyite and ringwoodite and high pressure phases of olivine.

Garnets are cubic aluminum silicates of the general composition $X_3Al_2Si_3O_{12}$, where X can be magnesium (pyrope), divalent iron (almandine), manganese (spessartine), calcium (grossular) (I have neglected garnets

where the Al is replaced by other trivalent cations). They are high pressure phases (by crustal standards) that are the product of metamorphism or deep burial.

Majorite is a high pressure tetragonal phase of (Mg,Fe)SiO₃ garnet.

Orthopyroxene is typified by enstatite, $(Mg_{1-x}Fe_x)SiO_3$, a chain silicate of orthorhombic structure.

Clinopyroxene is typified by the monoclinic diopside series Ca(Mg,Fe,Mn)Si₂O₆, another chain silicate.

Magnesiowüstite (now called ferropericlase) is magnesium-iron oxide $(Mg_{1-x}Fe_x)O$

Stishovite is a high pressure phase of silica (quartz), or SiO₂

Silicate perovskite is a high pressure distorted cubic form of magnesium-iron silicate, $Mg_{1-x}Fe_xSiO_3$. The magnesian end-member is now called bridgmanite.

Figure 12 shows laboratory studies for all the major minerals in the mantle, represented as Arrhenius fits to the original data. Most of these data were collected in a multi-anvil press, where large (by comparison with diamond anvil cells) samples can be made and solid state buffers for f_{O_2} used. The exception is the majorite measurement of Kavner et al., (not shown) which was carried out in a diamond anvil and extrapolated to mantle temperatures. This result disagrees radically from the ilmentite-garnet assemblage of Xu and Shankland, which should be a comparable measurement. The global induction measurements do not support the higher conductivity results.

Most minerals have activation energies between 0.5 and 2 eV (1 eV = 1.6×10^{-19} J/mole). It is interesting to note that upper mantle minerals have activation energies of around 1.5 eV, while lower mantle minerals (magnesiowüstite and silicate perovskite) have activation energies of 0.7 eV. Whether there is a reason or not for the high pressure phases to have lower activation energies, the implication is that the lower mantle will be more uniform in conductivity.

Note that these measurements are all nominally anhydrous. We will look at the water and mantle conductivity later.

Olivine conductivity. Olivine attracts special attention from the geophysics community, because it dominates the mineralogy of the mantle in the region that is easiest to study and closest to the crust. Because the next most abundant mineral, clinopyroxene, has a conductivity that is similar to olivine, it is fairly safe to build models of mantle conductivity on studies of olivine; many modifications of this approach have been proposed, in order to increase mantle conductivity to match field measurements that for one reason or another suggested a more conductive mantle, but we will start our discussions with dry, unaltered, olivine.

Figure 13 shows an early compilation of olivine conductivity. Although dated, this figure shows an interesting pattern. Jackson County dunite (JCD) and Red Sea peridot (RSP) are not mantle olivines, but have been metamorphically re-grown from talc. They seem to have a systematically lower conductivity. Other compilations suggest that there could be a difference between polycrystal samples and single crystal samples (San Carlos olivine, SCO, is a favorite single crystal olivine to study, but some studies have ground it up and re-formed sintered samples).



Figure 12. Laboratory studies of conductivity in nominally anhydrous mantle minerals, expressed as Arrhenius model fits to data. Solid lines represent the temperatures over which measurements were made; the broken and dotted lines are extrapolations to higher and lower temperatures. Ferropericlase data (dark blue) are from Dobson and Brodholt (2000). Perovskite results (dark blue) are from Xu *et al.* (1998, broken line) and Yoshino *et al.* (2008a, dotted line). Ringwoodite (black) is from Yoshino *et al.* (2008b, broken line) and Wadsleyite (also black) is from Yoshino and Katsura (2012, dotted line). Majorite garnet (red) is Yoshino *et al.* (2008c) for a pyrolite composition (dotted line) and mid-ocean ridge basalt composition (broken line). Garnet (light blue) results are from Xu and Shankland (1999, broken line) and Zhang *et al.* (2012, dotted line). Clinopyroxene (pink) is from Xu and Shankland (1999). Olivine SEO3 is from Constable (2006) for iron-wüstite (black, dotted line) and quartz-fayalite-magnetite (black, broken line) models of mantle oxygen fugacity.

Conduction mechanisms in olivine

The relationship between the major defect population in olivine and f_{O_2} is thought to be described by

$$8Fe_{Mg}^{\times} + 2O_2 \rightleftharpoons 2V_{Mg}^{''} + V_{Si}^{''''} + 4O_O^{\times} + 8Fe_{Mg}^{\bullet}.$$

Many studies indicate that the dominant charge carries are Fe_{Mg}^{\bullet} and $V_{Mg}^{''}$. For samples buffered by pyroxene, this model predicts that $[Fe_{Mg}^{\bullet}]$ and $[V_{Mg}^{''}]$ will each have a dependence on f_{O_2} of the form

$$[Fe^{\bullet}_{Mg}] = a_{Fe} f^{1/6}_{O_2} \quad ; \quad [V''_{Mg}] = a_{Mg} f^{1/6}_{O_2} \tag{2}$$



Figure 13. Olivine conductivity versus temperature, from Constable et al., 1992, JGR 97 p. 3397.

where the pre-exponential terms a are constant and [] denotes concentration. For mixed conduction, total conductivity is given by

$$\sigma = \sigma_{Fe} + \sigma_{Mg}$$
$$= [Fe^{\bullet}_{Mg}]\mu_{Fe}e + 2[V''_{Mg}]\mu_{Mg}e$$
(3)

where the μ are the respective mobilities for the charge carriers and e is the charge on the electron or hole.

Thermopower measurements provide a mechanism of estimating concentration independently of mobility, and Constable and Roberts (1997, Phys. Chem. Min., 24, p. 319) created a model of conduction in olivine based on a combined thermopower/conductivity data set. Figure 15 shows the data set used for this – a dunite from San Quintin in Baja California, Mexico. Natural rocks are useful samples because the crystallographic orientations are usually randomized, and there are enough minor phases to buffer the silica. It can be seen that the effect of f_{O_2} has the same magnitude as a 100 K change in temperature. Iron content also has an effect on polaron conduction, but Fe content in mantle olivines is quite constant at 10%.

Constable and Roberts used the models for thermopower and conductivity presented above, along with the expressions for mixed thermopower and conduction, to fit a parametric model of pre-exponential terms and



Figure 15 Data (symbols) and model fits (lines) for thermoelectric power and conductivity data for San Quintin dunite, as a function of f_{O_2} for three temperatures.

activation energies for mobilities

$$\mu_{Fe} = 12.2 \times 10^{-6} e^{-1.05 \ eV/kT}$$

$$\mu_{Mg} = 2.72 \times 10^{-6} e^{-1.09 \ eV/kT}$$

and concentrations

$$[Fe_{Mg}^{\bullet}] = b_{Fe}(T) + 3.33 \times 10^{24} e^{-0.02 \ eV/kT} f_{O_2}^{1/6}$$
$$[V_{Mg}''] = b_{Mg}(T) + 6.21 \times 10^{30} e^{-1.83 \ eV/kT} f_{O_2}^{1/6}$$

of the polarons and magnesium vacancies. (They included electrons as well, but this didn't fit the data.) The fitting required a weakly temperature-dependent terms representing an f_{O_2} -independent defect population, b_{Fe} and b_{Mg} , in order to fit the leveling of conductivity at low f_{O_2} . Although somewhat ad hoc, this behavior has been observed by many authors (e.g., Du Frane *et al.*, 2005). In all, the model contained 30 parameters.

This approach allows the contributions to conductivity to be separated for the two conduction mechanisms as a function of temperature and f_{O_2} . Figure 16 shows this for the three temperatures analyzed, along with an extrapolation to 1300°C, where it had been previously hypothesized that conduction mechanism changes. Below 1300°C, small polaron hopping (Fe_{Mg}^{\bullet}) dominates the conduction mechanism, and above 1300°C magnesium vacancies ($V_{Mg}^{"}$) account for conductivity.



Figure 16. Contributions from Fe^{\bullet}_{Mg} (red finely broken lines) and V''_{Mg} (blue coarsely broken lines) compared to total conductivity and thermopower (black solid lines) at four temperatures (1300°C is an extrapolation of the model).

Another interesting approach to obtaining mobility of charge carriers is to change the f_{O_2} in the sample environment rapidly (accomplished by changing the gas mix in a gas mixing furnace) and observing the reaction that generates charge carriers by observing conductivity during re-equilibration (Figure 17). The rate at which the sample comes to a new equilibrium exposes the mobility of the rate-limiting defect for the reaction. This need not be a charge-carrying defect, but Constable and Duba (2002: Phys. Chem. Min. 29 p. 446) showed that the mobilities of Fe_{Mg}^{\bullet} and $V_{Mg}^{''}$ could be estimated this way, and in fact agree well with the thermopower/conductivity modeling results.

Conductivity changes during diffusion re-equilibration can be modeled by standard diffusion theory de-



Figure 17. The change in conductivity as a result of changing gas mix (left) can be modeled to recover the time constant, and thus diffusivity/mobility of defects. This was done for two defects in olivine, and the result agrees well with mobilities determined by thermopower modeling (right).

scribing mass diffused after time $t(M_t)$ as a function of total mass after re-equilibration, M_{∞} .

$$\sigma(t) = \sigma_i + \sigma_s \frac{M_t}{M_\infty}$$

which for a regular solid can be expressed as

$$\sigma(t) = \sigma_i + \sigma_s \left[1 - c_1 \sum_{i=1}^{\infty} \frac{1}{c_2(i)} e^{-c_2(i)(t-t_o)/\tau} \right]$$

where c_1 and c_2 depend on the geometry and are known. The quantity τ is a time constant, which is related to diffusivity D by

$$\tau = l^2/D$$

where l is the grain size of the sample. Recall from the beginning of the course that mobility is related to diffusivity by the Nernst-Einstein equation:

$$kT\mu = qD$$

When the diffusivities derived from mobilities in the conductivity/thermoelectric power model are compared to diffusivities obtained by re-equilibration studies, the results are in remarkable agreement. The particularly interesting aspect of this is that the sample for the diffusion study was a lherzolite from Australia, quite different from the Mexican dunite.

Models of olivine conductivity

SO1 is a model of olivine conductivity derived by Shankland and Duba (1990) and based on a geometric average of Arrhenius fits to high temperature anisotropic single crystal measurements. The SO1 model is

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

It turned out that when you extrapolate SO1 to lower temperatures, it badly misfits the lower temperature olivine conductivity data. To correct this, SO2 (Constable, Shankland, and Duba, 1992) is a quantitative model of olivine conductivity based on a geometric average of the high temperature single crystal measurements of Shankland and Duba (1990), and lower temperature measurements on a polycrystalline olivine rock (a lherzolite, which would otherwise melt above 1250°C, fluxed by the pyroxene content). The SO2 model is

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

where the first term corresponds to low temperature behavior and the second term corresponds to a conduction mechanism that becomes dominant above 1300°C. The second conduction mechanism is inferred from the slight curvature of the high temperature σ -T curves, and a change in sign of thermoelectric power at around 1300°C.

SO2 served as a useful benchmark for some time, but was often found to under-predict mantle conductivity at the higher temperatures. Part of the problem is that in order to measure olivine conductivity at temperatures higher than 1200°C one must use single crystal measurements. This means that the anisotropy has to be incorporated into the model, but more importantly, pyroxene buffering of silica, which occurs in the natural polycrystalline samples, cannot be used without melting the sample because of the lower melting point of pyroxene. Indeed, although not reported in the literature, the single crystal sample of Shankland and Duba (1990) underwent some partial melting.

Not being able to make reliable measurements above 1200° C is a problem because the change in conduction mechanism from polarons to magnesium vacancies occurs around 1300° C (Schock *et al.*, 1989). There seems little one can do short of relinquishing the fine control on oxygen fugacity (f_{O_2}) obtainable in one-atmosphere gas mixing furnaces by resorting to high pressure measurements to inhibit melting. However, since f_{O_2} exerts a significant effect on olivine conductivity, that also presents some problems.

The solution to this was to use the Boltzmann physics-based defect model developed by Constable and Roberts (1997) and extrapolate this to higher temperatures, which should be more reliable than extrapolating parametric fits to the data. Constable (2006) used the mobilities and concentrations as a function of temperature and f_{O_2} from the joint conductivity/thermopower model to create a new quantitative model of conductivity, SEO3 (Figure 18). This model also allows explicit designation of the f_{O_2} conditions; although the quartz-fayalite-magnetite buffer is often used for the upper mantle, it is possible that at depth f_{O_2} may be lower, closer to the iron-wüsite buffer (McCammon, 2005). The effect of pressure is neglected in these models, but Xu *et al.* (2000) show that it is small compared with the sample-to-sample variations associated with high pressure measurements.

Although based on data at only 1000, 1100, and 1200°C, the above model is closely tied to the physics of conduction and correctly predicts equal contributions of polarons and vacancies at 1300°C. The data set upon which the model is based has advantages over the single crystal measurements; the low temperatures provide some insurance against sample alteration, the natural polycrystal averages over the three axes of olivine (dry olivine conductivity is weakly anisotropic), and the sample is naturally buffered for silicon. We only need a way to extrapolate the b_{Fe} and b_{Mg} terms to generate a new olivine σ -T relationship, which is done by fitting a linear relationship in log[]-1/T space to the original b at the three temperatures, yielding

$$b_{Fe}(T) = 5.06 \times 10^{24} e^{-0.357 \ eV/kT} \tag{4}$$

$$b_{M_e}(T) = 4.58 \times 10^{26} e^{-0.752 \ eV/kT} \quad . \tag{5}$$



Figure 18. The SEO3 olivine conductivity–temperature model for two different f_{O_2} conditions, quartz-fayalite-magnetite (SEO3-QFM) and iron-wüstite (SEO3-IW) (Constable 2006). For comparison the SO2 model of Constable et al. (1992) is also shown, as well as the San Carlos olivine model of Du Frane *et al.* (2005) (GM). The models are represented in both 1/T space (B) and temperature space (A).

Finally, we need to specify an $f_{O_2}(T)$ model; the quartz-fayalite-magnetite buffer is often used for the mantle, but for comparision we also make calculations for the iron-wüstite equilibrium. The results are shown in Fig. 13.8 as SEO3-QFM and SEO3-IW. To make it easy to relate the calculations to field observations, resistivity versus temperature is presented, but a plot of conductivity versus reciprocal temperature is also given to show the effective activation energies.

We see a reasonable agreement between SEO3 and SO2 below 1000°C, with the new model about a factor of 2 less conductive; the agreement in activation energy supports the validity of extrapolating the new model a considerable distance in 1/T. Above 1200°C the SEO3-QFM model is significantly more conductive than SO2, addressing the concerns that motivated this work. The model is also significantly more conductive at high temperature than the recent results of Du Frane *et al.* (2005), which, like SO2, are based on single crystal olivine measurements lacking a pyroxene buffer. Du Frane *et al.* used iron-doped electrodes to avoid iron loss from the sample to the electrodes, and observed that this may account for a $10^{0.15}$ increase in conductivity over previous measurements. Iron loss to electrodes could well have been a problem with the high temperature data upon which SO2 was based. It is not clear whether this effect is important at the lower temperatures of the dunite measurements, but the new model could be made slightly more conductive by the suggested amount. At temperatures below about 1300° C the Du Frane *et al.* data and model are up to one order of magnitude more conductive than most other observations made on olivine. They attribute this to a larger b_{Fe} term at lower temperatures; why this should be so requires further study.

At transition zone temperatures of around 1400°C, SEO3 predicts a significant dependence of conductivity on f_{O_2} (a factor of 3 for the two buffers shown in Figure 18). Since mantle f_{O_2} may decrease towards the transition zone (e.g. McCammon, 2005), this could be an important and observable effect, resulting in a decrease in conductivity with depth if the temperature gradient is small, or an uncertainty of about 100 K in temperature if f_{O_2} is not taken into consideration. *Oceanic Crust and Mantle.* Estimates of oceanic mantle conductivity come from magnetotelluric measurements carried out on the seafloor, and large-offset frequency domain controlled source EM (CSEM) experiments.

The dipole-dipole CSEM method was developed by Charles Cox in the early 1980's in order to study the electrical conductivity of the parts of the crust and mantle too shallow for study with marine MT. The higher frequency MT source fields are severely attenuated on the deep seafloor by the overlying seawater, and so the MT method is limited to long periods (usually 1,000 seconds and longer) and deep structure (a hundred kilometers or more). A transmitter is towed close to the seafloor, in order to couple well to the resistive seafloor rocks; the skin depth at 1 Hz in seawater is about 270 m and so little energy propagates through the water, whereas seafloor receivers at some distance from the transmitter detect energy that is representative of the more resistive seafloor. Using experiments such as these, source–receiver spacings of nearly 100 km have been achieved, resulting in sensitivity to structure as deep as 30 km or more. These experiments have helped constrain crustal structure, and have shown that the high resistivities of the lower crust extend into the oceanic mantle, at least away from ridges and volcanoes. The mantle appears highly resistive (10,000 Ω m or more) to depths of about 30 km, where thermally activated conduction in olivine should begin.



Two large-offset CSEM models (left), with SERPENT data (right).

Marine MT in 1D is blind to such highly resistive structure in the shallow part of the section, and early marine MT studies did not recognize that a resistive upper mantle will interact with the coastlines to depress electric fields on the seafloor and bias apparent resistivities low. When interpreted in terms of 1D models, such responses inevitably result in models with a highly conductive upper mantle. Correct interpretation of marine MT data requires 2D and 3D modeling, and even then is difficult because of the huge size of the ocean basins. However, when such modeling is carried out, we see that the MT data are compatible with the resistive upper mantle identified by the CSEM studies, and show the resistivity begins to decrease a few hundred kilometers deep and continues to decrease to the lower mantle. Not only does the interaction of the TM mode MT fields with bathymetry allow one to infer resistive upper mantle structure, it may even highlight the existence of conductive leakage paths between the ocean and conductive deeper mantle.

The most significant conductivity feature on the surface of Earth is the world ocean. Fortunately, the ocean is also the most easy feature to characterize. Global maps of bathymetry are available, and seawater conductivity is well defined as a function of salinity (nearly constant) and temperature. At mid and equatorial



2D MT inversions from the East Pacific Rise, west of Hawaii, and the Nicaraguan subduction zone.

latitudes, the surface water is warm and more than 5 S/m, but both temperature and conductivity drop rapidly below the thermocline. By a depth of 1,000 m, the conductivity is close to that observed at full ocean depth, and a value of 3.3 to 3.5 S/m is usually used to represent ocean conductivity. Occasionally you will see a value of 5 S/m, more representative of surface water, used for the entire ocean – this is wrong.



Expendable bathy-thermograph (XBT) taken in the Pacific Ocean near the ridge at 9° N. The temperature profile has been converted to electrical conductivity. The " \circ " symbols show the values near the seafloor in the deep ocean (4,000 – 5,000 m).

The rocks of the oceanic crust are, by and large, also fairly easy to characterize because for the most part the genesis of oceanic crust is uniform and the metamorphic history fairly simple. Boreholes to a depth of a kilometer or so, along with marine controlled source EM studies, provide *in situ* measurements of conductivity, which, combined with our knowledge of oceanic geology gleaned from dredging and ophiolite studies allows us to paint a fairly good picture of electrical structure in the oceanic crust. Away from ridges, the conductivity is basically a measure of the porosity of the volcanic and igneous rocks that make up the crust. Near ridges conductivity is increased by the presence of magma and hydrothermal fluids in the crust.

Pelagic sediments are around 1 Ω m and are underlain by extrusive basalts of about 1–10 Ω m. The intrusive dike system beneath the basalts is a little more resistive, perhaps 10–100 Ω m, but the gabbros are very much more resistive, 10⁴ Ω m or more. This high resistivity extends into the cool, dry upper mantle.





Global Conductance Map.

The electrical structure of the continental crust (which includes the continental shelves) is very much more complicated than the oceanic section, undoubtedly because it is better studied than the oceanic crust, but mostly because the geological history is much more complicated and the variation in water content (and salinity) is much larger. Data for crustal conductivities on the continents comes mainly from broadband and long period MT soundings, with some data from large-scale CSEM and resistivity studies.

Neglecting the details, and ignoring unusually conductive, volumetrically small, and often economically significant minerals, we gan make some gross generalizations:

Continental shields: $10^3 - 10^6 \Omega m$ Continental sediments: $10 - 100 \Omega m$ Marine sediments: $1 - 100 \Omega m$

Everett et al. (2003: GJI, 153, p. 277) formalized this approach to generate a global crustal conductance map, using the global sediment thickness map of resolution of $1^{\circ} \times 1^{\circ}$ compiled by Laske and Masters (1997: Trans. AGU, 78, F483, 1997), based on an earlier $5^{\circ} \times 5^{\circ}$ map of Mooney et al. (1998: JGR, 103, p. 727). This map contains sediment density, V_P , and V_S discretized in up to three layers; a surface layer up to 2 km thick, an underlying layer up to 5 km thick, and, where necessary, a third layer to make up total sediment

thickness, which often exceeds 10 km.

The sediment map was augmented by a $1^{\circ} \times 1^{\circ}$ topographic/bathymetric map. The world was divided into three regions based on topography; (i) the ocean basins and continental shelves defined by elevations below sea level, (ii) the coastal plains and low-lying continental sedimentary basins defined by elevations above sea level but below 100 m, and (iii) the continental interiors and highlands above 100 m elevation.

In region (i), the oceans, the ocean layer was assigned a conductivity of 3.2 S/m (0.3 Ω m), the upper two sediment layers (up to 7 km thick) were assigned a conductivity of 0.8 S/m (1.25 Ω m), and the deepest sediments assigned a conductivity of 0.02 S/m (50 Ω m).

In region (ii), the coastal plains and low basins, the entire sedimentary section was assigned a conductivity of 0.5 S/m (2 Ω m).

In region (iii), the continental highlands, the entire sedimentary section was assigned a conductivity of 0.03 S/m (33 Ω m).

The balance of the section to a depth of 50 km, representing oceanic and continental igneous rocks, was assigned a conductivity of 0.001 S/m (1000 Ω m).



A Crustal Electrical Conductivity Model

Algorithm used by Everett et al. (2003) to generate a global conductivity map. Blue is igneous basement, light blue, light brown and light pink represent sedimentary basins, and dark pink ocean.

Total conductance is easily generated by summing the conductivities and thicknesses of the various sections. For frequencies where the skin depth is large compared with the thickness of a layer, a surface layer can be characterized by its conductance only, because its thickness cannot be resolved and attenuation of EM energy is determined entirely by the conductivity–thickness produce, or conductance. Computations in three dimensions often exploit this phenomenon using a *thin-sheet algorithm*.

The above formula is undoubtedly arbitrary and could be improved upon, but improves on simple ocean depth as a proxy for conductance. Overall, the sedimentary sections defined in this way contribute only 10% to the total surface conductance, but in areas such as the Gulf of Mexico, Arctic Ocean, and Mediter-

global surface conductance map, logarithmic scale [log10 S]



Global electrical conductance generated by the crustal algorithm of Everett et al. (2003).

ranean/Caspian/Black Seas, accumulated sediment has a conductance comparable to the oceans and sediments drastically alter the shape of the continent/ocean function.

Global Mantle Conductivity

Although marine EM studies are technologically challenging, the crustal heterogeneity of the continents presents a great hurdle to estimating mantle conductivity. Very long period MT studies, such as that of Egbert and Booker (1992, JGR 97 p. 15,099), are limited by the lack of long period E-field signals and unknown static, or electrode, effects of the E-field dipoles, making absolute determinations of resistivity difficult. The traditional way is to calculate GDS functions from magnetic observatory data, which although dependent on the P_1^0 source field assumption, can extend to periods of at least several months and provide absolute estimates of resistivity. Figure 14.9 shows an example of these GDS responses, computed by two different groups, along with an average response and inversions. At short periods scatter between observatories is probably due to local variations in crustal structure. At long periods, scatter may be caused by a breakdown of the P_1^0 assumption, because grouping is tightest at the solar rotation period of 27 days. Constable (1993: JGG, 45, p. 707) averaged the GDS responses from these two studies to create a global average, hopefully sensitive to average radial structure, using the original scatter in the data to compute standard errors in the means. The resulting response is remarkably consistent with a 1D model, in that D^+ fits the data to RMS 0.93. Figure 14.9 also shows the inevitable tradeoff between data misfit and model roughness.

Figure 14.10 illustrates various issues associated with interpreting the global response functions. Firstly, we note that the global average generated by Constable (1993) and a broader band, purely European GDS study by Nils Olsen are in remarkable agreement. Admittedly, the observatory distribution is still biased towards Europe, but there were significant differences in the data and methods used. Secondly, although the smoothest model fitting the data starts to increase in conductivity in the transition zone, these data can be fit with a remarkably simple model of an upper mantle about 200 Ω m and a lower mantle of about 1 Ω m. This illustrates that the jump in conductivity at the 670 km discontinuity is one of the largest conductivity model generated by Xu et al., based purely on laboratory measurements and assumptions of temperature and mineralogy, was deemed acceptable because it appears quite close (in model space) to similar (overfit, in my opinion) smooth models that had been published. However, if one runs the Xu et al. model forwards,



TOP: Magnetic observatories used to compute GDS responses by Roberts (1984: JGRaS, 78, p. 547), squares, and Schultz and Larson (1987: JGRaS, 88, p. 733), triangles. MIDDLE: Compiled responses from the Roberts study (diamonds) and the Schultz and Larson study (triangles). BOTTOM: Averaged observatory responses with D^+ best fit (left) and D^+ model along with smooth models of various misfit (right).

it clearly does not fit the data. One explanation for this is that the more conductive phases in the transition



Response functions (left column) from European observatories (Olsen, 1999: GJI, 138, p. 179) and a global compilation (Constable, 1993: J. Geomag. Geoelect., 45, p. 707). Model (A) is a simple Occam's inversion of the data (red) or a similar inversion with a jump in conductivity at 670 km deep allowed (blue). Model (B), shaded, shows a Xu et al. laboratory model (Xu et al., 1998: Science, 280, p. 1415), and its response (which clearly does not fit the data). Xu et al. (2000, JGR 105 p. 27,865) reduced their estimate of transition zone conductivity, but their more recent model is still close to the lower limit of the earlier one.

zone are texturally isolated by a phase that continues to be relatively resistive.

Medin, Paker, and Constable (2006, PEPI, 160, p. 51) went even further with this data set by using a quadratic programming algorithm to estimate bounds on conductivity within each of the major seismic/mineralogical regions of the mantle. Figure 14.11 shows the data set used in this study, which differs from Figure 14.10 only by the exclusion of four admittances which failed to satisfy the assumption of one-dimensionality (three of which they had reason to believe did not meet the source-field requirements), and the inclusion of a (rather old and dubious) 11-year solar cycle datum.

Figure 14.12 shows various inversions of this data set. The green lines represent the D^+ model of Parker and Whaler (1981), scaled by 10^5 and fitting the data to RMS 1.044. The red line is a smooth, first derivative regularized inversion fitting the data to RMS 1.2, and the blue line is a similar inversion but allowing un-penalized jumps at the 440 km and 670 km seismic discontinuities. Finally, the yellow boxes are bounds on average conductivity at the 90% confidence level over the depth intervals 0–418 km, 418–672 km, and



Figure 14.11. Response function used by Medin *et al.* (2006), consisting of the slightly edited data sets from Olsen (1999, open symbols) and Constable (1993, solid symbols). Real component is plotted as circles, the imaginary as triangles. The error bars are as reported by the authors. The red line is the response of the smooth model shown in Figure 14.12, fitting the data to a conservative RMS 1.2.

672–1666 km. The broader bounds put no restrictions on the models, the tighter bounds shown in the darker color restrict the models to be monotonically increasing in conductivity with depth.

These models are representative of the many mantle conductivity profiles published in the literature. One of the most well-resolved features is the jump in conductivity to 2–3 S/m in the lower mantle, entirely consistent with the more recent measurements on silicate perovskite (see Figure 13.2). The uppermost mantle above the transition zone is likely to be quite heterogeneous and dependent on local tectonic setting (e.g. ridges, subduction zones, plumes could all be expected to be locally much more conductive), but the global average conductivity of 50–100 Ω m is a good agreement with dry olivine conductivity. The order of magnitude increase of conductivity in the transition zone is in general agreement with laboratory measurements on the high pressure phases wadsleyite and ringwoodite, although biased towards somewhat lower conductivity. This mentioned before, this is easily explained in terms of mixing with more resistive phases such as garnet and pyroxene. The order of magnitude increase in conductivity in the lowermost mantle is just within the range of thermally activated conduction in perovskite, or could be the influence of other mineral phases. The increase is poorly constrained, relying on the longest period measurements having largest uncertainty, and probably represents a lower bound on conductivity because the smoothness penalty minimizes slope.

Water and Other things in the Mantle

Factors affecting olivine conductivity. We see from our previous lectures that the electrical conductivity of dry olivine at room pressure is extremely well characterized. The pressure effect is small, and given the problems in controlling f_{O_2} under pressure, perhaps too small to be usefully quantified. So the real question at this point is whether dry olivine, exemplified by, for example, the SEO3 model, is indeed representative



Figure 14.12. Models fitting the data set shown in Figure 33. Green lines are the D⁺ model divided by 10^5 , red line is a first-deriviative maximally smooth model, and the blue line is a smooth model that is allowed to jump at 440 km and 670 km. The yellow boxes represent bounds on average conductivity from Medin *et al.* (2006). Values of selected mineral conductivities from Figure 26 are also shown.

of the upper mantle. Early estimates of mantle conductivity from marine MT studies were biased towards conductive values by the coast effect, which led to a scramble to reconcile the relatively higher resistivities of silicate conductivities with these field measurements. The field studies now tend to suggest higher resistivities, which to my mind are more realistic, and are as often as not compatible with the SEO3 model, but there remains a passion for increasing mantle conductivity. No doubt some or all of these mechanisms will be shown to be contributors, even if only to minor extent. We review them here.

Melt. Since magma is very much more conductive than sub-solidus olivine, one mechanism for increasing conductivity is to invoke a mantle permeated by partial melt. Tholeitic melt conductivity is also a thermally activated phenomenon, given by

$$\sigma = 10^{5.332} e^{-1.533 \text{eV}/kT} \text{ S/m}$$

(Tyburczy and Waff, 1983: J.G.R. 88, p. 2413). For small melt fractions to be effective mechanisms for increased conduction, the melt must be well connected, and so one model for binary mixing that would be appropriate in this case would be the connected tube model of Grant and West. Figure 1 shows this model for various fractions of partial melt as a function of temperature. Bear in mind that well-connected melt is gravitationally unstable, and will migrate upwards, and so while partial melt is clearly an important mechanism in volcanic systems and mid-ocean ridges, it is not clear that the residency time in the mantle is long enough for it to contribute to ubiquitous enhancement of conductivity.

Recently, it has been shown that carbonate-rich melts can be as much as an order of magnitude higher conductivity than silicate melts. This effect is greatest at low melt fractions in deeper parts of the mantle. As the melting progresses, silicate content rises and the conductivity drops towards that of pure silicate melts.

Carbon. Graphite is extremely conductive $(10^4 - 10^6 \text{ S/m})$, and so it would take only a small amount to



Figure 1 Electrical conductivity of olivine plus well connected partial melt.

increase mantle conductivity over that of SO2, as long as it is well connected. This is possible; there is a significant amount of carbon in the mantle (several hundred ppm) that can exist as CO_2 fluids or graphite. Movement between the two is up to our old friend f_{O_2} , and so it is conceivable that CO_2 fluids permeating grain boundaries could be reduced to form a connected network of graphite. The idea that carbon might contribute to mantle conductivity was put forward by Duba and Shankland (1982: GRL, 9, p. 1271). There is a big limitation on carbon as a conduction mechanism for mantle rocks; below about 160 km graphite turns into diamond, which is a non-conductor. Note also that carbon has a low thermal activation energy, so we would not expect to see an increase in conductivity with temperature/depth for carbon-enhanced conductivity.

Strain-induced defects. Since the early marine MT purported to see a zone of increased conductivity at the depth of the asthenosphere, one possibility was that straining generated defects that contribute to conduction. This idea was dispelled by careful measurements of Hirsch and Wang (1986: JGR, 91, p. 429).

Oxides and sulfides. Mantle rocks typically contain about one percent oxides of iron, chromium, and titanium, but as discrete crystals these do not contribute to bulk conductivity in spite of their high mineral conductivities. It is possible to increase the magnetite content of mantle rocks by hydration, as discussed above, but there is no field evidence of increased mantle conductivity as a result of this alteration.

Ducea and Park (2000) interpreted high mantle conductivities under western North America as connected sulfide melts at concentrations of less than 0.4 vol%. Watson *et al.* (2010) showed that even at 1 vol%, iron sulfide in polycrystalline olivine was largely unconnected, consistent with estimated percolation threshold of 4–6 vol%. However, they did observe an increase in conductivity to about 0.1 Sm⁻¹ at 900°C, inferred



Figure 1b Electrical conductivity of carbonate melts compared to other mantle materials, from Gaillard *et al.* (2008).

to be the result of a very small amount of interconnection or an increase in the surface conduction of olivine grains. This is sufficient to explain many observations of increased mantle conductivity which have traditionally been interpreted as melt or the effect of water.

Water. Like carbon, water is known to exist in the mantle – estimates are that several Earth oceans are still resident somewhere in the deep Earth. Where, and in what state, is less well understood. Recent high pressure measurements on Ringwoodite and Wadeslyite suggest that water solubility in these minerals is very much higher than in upper or lower mantle minerals, leading Bercovici and Karato (2003: Nature 425, p. 39) to suggest a water-saturated transition zone (440–670 km deep) and pooling of water and melt at the 440 km discontinuity.

There are 3 ways to store water in the mantle: free water, hydrous minerals, and defects in minerals (i.e. dissolved directly in the mineral lattice). Free water could exist for a period of time in the coolest parts of the mantle, but at even modest temperatures will eventually react with olivine to create serpentine, a talc-like mineral. This mechanism is interesting in that magnetite is excluded during the reaction, creating halos of fine magnetite around relic olivine grains that can be electrically connected and lower the resistivity of the rock considerably (Stesky and Brace, 1973: JGR 78, p. 7614). However, hydrous minerals are not otherwise conductive (consider; mica is a hydrous mineral once used as a high-voltage insulator).

At some temperature/pressure, depending on the mineral but generally at depths shallower than 125 km, hydrous minerals will decompose to produce free water, which is not stable and will usually lower the melting point sufficiently to generate a partial melt into which it dissolves, which will in turn be gravitationally unstable and migrate upwards.



It all started in 1990...

The idea that water dissolved in olivine could enhance electrical conductivity was proposed by Karato (1990: Nature 347, p. 272), based on observations that chemical diffusion of hydrogen in olivine was very high, particularly (only) along the a-axis (the activation energy is 1.3 eV; not dissimilar to other upper mantle conductors). This was initially put forward as an explanation for early marine MT measurements that were almost certainly biased low by the effect of coastlines, but has found an enthusiastic following in the community. Although the effect is not as dramatic as Karato proposed when the effect of the other two axes is taken into account (adding about 1,000 ppm hydrogen per silicon atom increases conductivity about an order of magnitude over SO2), since the a-axis is considered to be aligned with mantle flow, the hydrogen hypothesis predicts significant anisotropy in the upper mantle (only about 100 ppm is required to increase a-axis conductivity by an order of magnitude). Some field studies claim to see such an anisotropy, but in my opinion the results are equivocal. While observation of anisotropy in MT data quickly led to support for the idea of hydrogen conduction, many things can result in anisotropic MT responses; for example, structural anisotropy outside the study area could be difficult to identify without adequate data.

The effect of hydrogen on upper mantle conductivity rapidly became a matter for debate. Direct laboratory evidence for enhanced conduction by hydrogen was slow to appear and initial reports were in poor agreement with each other and with the diffusion data (e.g. Shankland and Duba, 1997; Poe *et al.*, 2005; Wang *et al.*, 2006; Yoshino *et al.*, 2006), suggesting that hydrogen does not behave as a simple charged defect in olivine. More recent results have not completely resolved this issue, and there is an order of magnitude or more discrepancy between various studies (Figure 2A). Yoshino *et al.* (2009) argue that the higher temperatures used by Wang *et al.* resulted in dehydration and increased conductivity from water on grain boundaries or the sample cell. Poe *et al.* (2010) also cite differences in the way water content is estimated and the type of calibration used for this, arguing that a factor of 4 difference with Yoshino *et al.*'s result could be explained



Early results of hydrous olivine conductivity, from Yoshino et al. (2006) (left) and Wang et al. (2006) (right).

in this way. However, Wang *et al.* (2006) used the same analytical method as Yoshino *et al.* (2006; 2009) and still obtained differing results. Poe *et al.* also note other differences in sample type and pressure. Because the activation energy for the hydrated samples is lower than for dry olivine, the influence of water will decrease with temperature (and depth). The few results on other hydrated upper-mantle minerals, garnet and pyroxene (Figure 2B) show a similar pattern.

High pressure measurements on the transition zone minerals ringwoodite and wadeslyite suggest that water solubility in these minerals is very much higher than in upper or lower mantle minerals, leading Bercovici and Karato (2003) to suggest a water-saturated transition zone (410–670 km deep) and pooling of water and melt at the 410 km discontinuity. Furthermore, Huang *et al.* (2005) showed that conductivity is enhanced by the addition of water in these minerals. This presents the exciting possibility that electromagnetic methods can provide important constraints on deep Earth processes. Based on conductivity bounds obtained from a rigorous analysis of global response function data, Medin *et al.* (2006) estimated that the global average water content in the transition zone is < 0.27%, less than the 0.4% required for pooling at the 410 km discontinuity. However, there remains the possibility that the effect of water is heterogeneous and more significant locally (e.g. Toffelmier and Tyburczy, 2007), and Medin *et al.*'s inferences depend critically on the early laboratory data. More recent laboratory work (Figures 2 C, D), however, echos the olivine story; different groups and laboratories produce results that differ by up to an order of magnitude. Again, Yoshino and his colleagues produce lower conductivity results and caution against making measurements at high temperatures where water is more labile.

What do the global sounding data tell us about water in the mantle? Figure 3 shows a the data set used in an inversion study by Medin *et al.* (2006). These data consist of a combination of stacked global observatory GDS responses (Constable, 1993a) which relied on assumptions of P_1^0 geometry, and European observatory responses of Olsen (1999) which allowed more complicated source field geometry and thus a broader bandwidth. Medin *et al.* excluded four admittances which failed to satisfy the assumption of one-dimensionality, three of which they had reason to believe did not meet the source-field requirements.

Figure 4 shows various inversions of this data set. The green lines represent the D^+ model of Parker and Whaler (1981), scaled by 10^5 and fitting the data to RMS 1.044. The red line is a smooth, first derivative



Figure 2. Laboratory studies of conductivity of mantle minerals under pressure, containing 0.1 weight percent water (red) or 1 weight percent water (blue) as point defects, and shown as Arrhenius model fits to data. Green curves are for anhydrous models. Solid lines represent the temperatures over which measurements were made; other lines are extrapolations to higher and lower temperatures. In all plots, the black lines are the SEO3 models shown in Figure 26, shown to provide a common reference. A: Olivine models from Wang *et al.* (2006), Poe *et al.* (2010), and Yoshino *et al.* (2009). Anhydrous data are from Yoshino *et al.* (2009). B: Other upper mantle minerals from Dai and Karato (2009a) and Zhang *et al.* (2012). C: Wadsleyite from Huang *et al.* (2005), Romano *et al.* (2009), Dai and Karato (2009b), Yoshino *et al.* (2012) and Yoshino *et al.* (2008b). Dry models are from Romano *et al.* (2009), Yoshino *et al.* (2008b), and Yoshino *et al.* (2012). D: Ringwoodite from Huang *et al.* (2005) and Yoshino *et al.* (2008b).

regularized inversion fitting the data to RMS 1.2, and the blue line is a similar inversion but allowing un-penalized jumps at the 440 km and 670 km seismic discontinuities. Finally, the yellow boxes are bounds on average conductivity at the 90% confidence level over the depth intervals 0–418 km, 418–672 km, and 672–1666 km, derived by Medin *et al.* (2006). The broader bounds put no restrictions on the models, the tighter bounds shown in the darker color restrict the models to be monotonically increasing in conductivity with depth. The figure also shows the electrical conductivities of dry mantle minerals discussed in the last lecture, which are, by and large, compatible with the models. On the other hand, some of the lower estimates of wet transition minerals would also be compatible with these models.



Bercovici and Karato, 2003, argue that water in the transition zone will cause melting at the base of the upper mantle.

Of course, you all know that inversion is non-unique by now. A stronger approach is to exclude possible models. Figure 5 tests one of the more extreme mantle water filter models and shows that it is not compatible with the data (although we could try modifying the background model to compensate, we would then lose our good agreement with the rest of the mantle mineral data, and the biggest conductor you can hide this way is 10 times smaller).

The current proposals for water pooling in the transition zone provide a great opportunity for geomagnetic induction methods to make fundamental contributions to our understanding of the mantle. Although, based on average conductivity, a case can be made that water pooling does not occur, there is every reason to believe that the distribution of water is not homogeneous, and that locally water may reach the critical threshold. Long period MT soundings, if they can be made free of distortions due to large scale crustal structures, could provide important constraints on this hypothesis. Satellite and observatory response functions, if generated in a way that does not reject 3D structure, could also be bought to bear on this problem.

The Core

The state of the art with regards conductivity of the core used to be nicely summarized in the recent paper by Stacey and Anderson (2001: PEPI, 124, p. 153). Their estimates are $2.1 \times 10^{-6} \Omega m$ in the outer core and $1.6 \times 10^{-6} \Omega m$ in the inner core. This is a refinement on the previously accepted values $(1-3 \times 10^{-6} \Omega m)$.

Then this world order was upturned when computer modeling and diamond anvil cell measurements updated these estimates to $1.3 - 1.6 \times 10^5$ Sm⁻¹ or resistivities of $6-7 \times 10^{-6}$ Ω m, three times the shock wave values. This is not terribly significant in terms of geoelectromagnetism, but it is important with respect to thermal conductivity, which is linearly related to conductivity times temperature, and the age of the inner core (now much younger that previously thought).



Figure 5.A forward model exercise testing the Bercovici and Karato hypothesis – a 10 km, 0.1 S/m layer at the base of the upper mantle.

Resistivity of metals increases with temperature because lattice vibrations (phonons) can be considered to scatter electrons. Similarly, adding impurity atoms also increases scattering and resistivity. This is important because we know the outer core is alloyed with 10–25% light elements for the alloyed iron to match density estimates. The argument is that the effects of impurities are independent of temperature, and indeed somewhat independent of the actual impurity chemistry; the effect of Si and Ni (both probably present in the core) are considered similar when measured in weight %.

Iron behaves as an "ideal" metal in that the effect of pressure acts to decrease lattice vibrations in a way that affects melting point and resistivity similarly, and so iron at the melting point T_M is expected to have the same resistivity $(1.35 \times 10^{-6} \ \Omega m)$ whether at zero pressure or at core pressure. At other temperatures T for a given pressure, resistivity is assumed to be proportional to T/T_M . Thus at the core-mantle-boundary (CMB), temperature is estimated to be 3750 K and iron solidus as 4147 K, so the component of pure iron resistivity is $\rho = 3750/4147 \times 1.35 \times 10^{-6} \ \Omega m$ or $1.22 \times 10^{-6} \ \Omega m$. At the inner core boundary, temperature is estimated to be 4971 K and iron solidus as 6000 K, so the component of pure iron resistivity is $1.12 \times 10^{-6} \ \Omega m$.

Because iron converts from body-centered cubic (bcc) to hexagonal close packed (hcp) under pressure, measurements of iron with impurities have been carried out using shock wave experiments. In a shock wave experiment, a gas/explosive gun or laser is fired at a sample. The shock front, moving at velocity u_s , separates material at the starting density, pressure, and temperature (ρ_o , P_o , T_o) with material at the shocked



Only a few hundred parts per million water lowers mantle solidus by 100°C. From Hirschmann *et al.* (2008). conditions (ρ , P, T). The shock front is supersonic; it moves faster than the actual material, or sound, speed u_p .

Conservation of mass across the shock front gives

$$u_s \rho_o = \rho(u_s - u_p)$$

so the density increase produced by the shock is

$$\frac{\rho}{\rho_o} = \left(1 - \frac{u_p}{u_s}\right)^{-1}$$

and pressure is given by the rate of change of momentum per unit area of shock front, which for material starting at rest and room pressure is

$$P = \rho_o u_s \times u_p$$

So, knowing the ratio and product of the two velocities for various sized shocks gives density as a function of pressure for the material.

The shock compression is not adiabatic because the material gains kinetic energy. The temperature curve which the material follows during shocking is called a Hugoniot.

Stacey and Anderson fit linear models to shock-wave data to conclude that a silicon impurity of volume fraction X would contribute $3.0X \times 10^{-6} \Omega m$ to resistivity. They expected the silicon to exsolve in a similar way to nickel, and so took averages of the two components to finally come up with an impurity contribution of $0.9 \times 10^{-6} \Omega m$ for a total resistivity of $2.1 \times 10^{-6} \Omega m$. They guesstimated the lower impurity content of the inner core to derive a total resistivity of $1.6 \times 10^{-6} \Omega m$.

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